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# Managing and Disposing of Residues from Environmental Control Facilities in the Steel Industry

**Dravo Corp, Pittsburgh, Pa**

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16. ABSTRACT The report gives results of a study of the management and disposal of residues from environmental control facilities in the steel industry. Information from 13 integrated U.S. steel mills is compared with that found in the literature and with data collected during visits to English, German, and Japanese steel mills, technical and industrial associations, and government agencies. Methods used to recycle dusts and sludges and to regenerate or recover waste acids and oils are covered. Of the approximately 16.6 million tons of residues, 9.1 million tons are recycled, and 7.5 million tons are dumped or stored for later reuse. The major reasons for not recycling the residues, aside from economics, are higher than tolerable tramp element contents (e.g., Zn, Pb, Na, K) or oil content, and the extremely fine residue consistency. The pollution control facilities used and the quantities and properties of the residues generated in the various processes are described. In 1974, the U.S. steel industry produced over 145 million net tons of raw steel. During the same period, over 16 million tons of pollution abatement residues were generated by the industry in 14 different iron and steelmaking subcategories, not including iron and steelmaking slags.

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| Iron and Steel Industry | Stationary Sources | 11F |
| Residues | | |
| Dust | | 11G |
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# MANAGING AND DISPOSING OF RESIDUES FROM ENVIRONMENTAL CONTROL FACILITIES IN THE STEEL INDUSTRY

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EPA-600/2-76-267
October 1976

# MANAGING AND DISPOSING OF RESIDUES FROM ENVIRONMENTAL CONTROL FACILITIES IN THE STEEL INDUSTRY

by

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# ABSTRACT

In 1974 the United States steel industry produced 145,720,000 net tons* of raw steel. During the same period, approximately 16.6 million tons of pollution abatement residues were generated by the steel industry in the U.S. This includes all residues arising in 14 different iron and steelmaking subcategories, but does not include iron and steelmaking slags.

The pollution control facilities used for air and water pollution control, the quantities and properties of the residues generated in coking, sintering, blast furnace (iron), blast furnace (ferro-manganese), basic oxygen furnace, open hearth furnace, electric arc furnace, vacuum degassing, continuous casting, rolling operations, pickling operations, coating operations, waste water treatment facilities, and boilerhouses as well as the management and disposal of the residues are described.

The information obtained during this study from 13 American integrated steel mills is compared with those found in the literature and with data collected during visits to English, German and Japanese steel mills, technical and industrial associations and government agencies.

A special section deals with recycling of iron and steelmaking pollution abatement residues. Methods used for recycling of dusts and sludges and the regeneration or recovery of waste acids and oils are covered.

Of the approximately 16.6 million tons of residues, 9.1 million tons are recycled, while 7.5 million tons are dumped or "stored for later reuse."

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* Although EPA policy requires the use of metric units, this report uses non-metric units for convenience in giving U.S. production figures. Readers are encouraged to use the conversion factors on page xi.

The major reasons for not recycling the residues, besides the economic factors, are the higher than tolerable tramp element contents (such as Zn, Pb, Na, K) or oil content, and the extremely fine consistency of the residues.

In spite of these problems in recycling, with the development of new technologies the trend is toward recycling not only most of the process waters but also most of the iron and other metal-containing residues as well as the waste acids and oils.

Chapter TABLE OF CONTENTS Page

Abstract iii
Table of Contents v
List of Figures vi
List of Tables vii
Conversion Factors and Abbreviations xi
Acknowledgement xii
I Conclusions and Recommendations 1
II Introduction 7
2.1 Purpose 7
2.2 Organization 8
2.3 Methods Used to Develop Information 9
2.4 General Description of the U.S. Steel Industry 11
2.5 Rationale for Subcategorization 18
2.6 General Description of Pollution Abatement Residue Generated 20
2.7 References 24
III Pollution Abatement in the Iron and Steel Industry Category, by Subcategories 25
3.1 Coking 26
3.2 Sintering 35
3.3 Blast Furnace (Iron) 47
3.4 Blast Furnace (Ferromanganese) 63
3.5 Basic Oxygen Furnace (BOF) 67
3.6 Open Hearth Furnace (OH) 80
3.7 Electric Arc Furnace (EAF) 91
3.8 Vacuum Degassing 100
3.9 Continuous Casting (CC) 104
3.10 Rolling 109
3.11 Pickling 127
3.12 Plating and Coating 133
3.13 Boilerhouses 136
3.14 Waste Water Treatment Plants 140
3.15 Miscellaneous Other Operations 153

Chapter TABLE OF CONTENTS Page

3.16 Recycling 156

Appendix Methods used in Analyzing Steel Industry Pollution Control Residues 174

FIGURES

II 2-I Steelmaking from Raw Materials to Finished Mill Product 17

III 3.1-I Biological Coke Waste Treatment Plant Schematic 30

3.14-I Waste Water Treatment Plant Schematic - Plant B 144

3.14-II Waste Water Treatment Plant Schematic - Plant D 145

3.14-III Waste Water Treatment Plant Schematic - Plant E 146

3.14-IV Waste Water Treatment Plant Schematic - Plant F 147

3.14-V Waste Water Treatment Plant Schematic - Plant G 148

3.14-VI Waste Water Treatment Plant Schematic - Plant H 149

3.14-VII Waste Water Treatment Plant Schematic - Plant I 150

3.14-VIII Waste Water Treatment Plant Schematic - Plant J 151

3.14-IX Waste Water Treatment Plant Schematic - Plant K 152

## TABLES

Chapter Page

II

2-1 Iron and Raw Steel Production in the U.S. 12

2-2 Blast Furnace Production 13

2-3 Raw Steel Production by Type of Furnace 14

2-4 Material used by Blast Furnaces in Manufacture of Iron (Pig and Molten) in 1974 15

2-5 Industry Consumption of Scrap and Pig Iron by Types of Furnaces 16

2-6 Categorization and Subcategorization of the Iron and Steel Industry 19

2-7 Quantities of Pollution Control Residues Generated in Various Iron and Steelmaking Operations 22

2-8 Estimates of Iron and Steel Mill Pollution Control Residues in the U. S. in 1974 23

III

3.1-1 Quantities of Coke Breeze and Coking Pollution Control Residues Generated in Steel Mills 31

3.1-2 Raw Residual Loads Associated with Coke Manufacturing Operations 33

3.2-1 Analysis of Sintering "Windbox" End Pollution Control Residues 39

3.2-2 Analysis of Sintering "Discharge" End Pollution Control Residues 40

3.2-3 Analysis of Sinter Plant Dust (from Literature) 41

3.2-4 Particle Size Analyses of Sinter Plant Residues 42

3.2-5 Types and Quantities of Residues Generated in U.S. Sintering Operations and their Disposal 44

3.2-6 Raw Residual Loads Associated with Sinter Plant Operations 45

3.3-1 Chemical Analyses of Blast Furnace Residues - Dust (Part 1) 52

Chemical Analyses of Blast Furnace Residues - Sludges (Part 2) 53

3.3-2 Chemical Analyses of Blast Furnace Residues (from the Literature) 54

3.3-3 Particle Size Distribution of Blast Furnace Dust and Sludges 55

| Chapter | | Page |
|---|---|---|
| 3.3-4 | Blast Furnace Dust and Sludge (Residues) Collected (1974) | 56 |
| 3.3-5 | Blast Furnace Residues Disposition - 1974 | 57 |
| 3.3-6 | Typical Ranges of Quantities of Residues Collected by BF Operations by Countries | 58 |
| 3.3-7 | Raw Residual Loads Associated with Blast Furnace Operations | 59 |
| 3.4-1 | Chemical Analyses of BF Ferromanganese Dust and Sludges | 64 |
| 3.4-2 | Particle Size Analyses of BF Ferromanganese Dust and Sludges | 64 |
| 3.5-1 | Chemical Analyses of BOF Residues - Fines | 70 |
| 3.5-2 | Chemical Analyses of BOF Residues - Sands | 71 |
| 3.5-3 | Chemical Analyses of BOF Residues (from Literature) | 72 |
| 3.5-4 | Particle Size Analyses of BOF Residues | 73 |
| 3.5-5 | BOF Sludge and Dust Collections - 1974 | 74 |
| 3.5-6 | BOF Residues Disposition - 1974 | 75 |
| 3.5-7 | Quantities of BOF Pollution Control Residues Collected by Countries | 76 |
| 3.5-8 | Raw Residual Loads Associated with BOF Steel Manufacturing Processes | 77 |
| 3.6-1 | Percent of Raw Steel Produced by Furnace Type | 80 |
| 3.6-2 | Chemical Analyses of Open Hearth Dusts | 85 |
| 3.6-3 | Chemical Analyses of Open Hearth Residues (from Literature) | 86 |
| 3.6-4 | Particle Size Analyses of Open Hearth Dusts | 87 |
| 3.6-5 | Quantities of Residue Generated in Open Hearth Steelmaking Operations | 87 |
| 3.6-6 | Raw Residual Loads Associated with the Open Hearth Steel Manufacturing Processes | 88 |
| 3.7-1 | Chemical Analyses of EAF Residues | 93 |
| 3.7-2 | Chemical Analyses of EAF Residues (from Literature) | 94 |
| 3.7-3 | Particle Size Analyses of EAF Residues | 95 |
| 3.7-4 | Quantities of Residues Generated in EAF Operations | 96 |

| Chapter | | Page |
|---|---|---|
| 3.7-5 | Raw Residual Loads Associated with EAF Steel Manufacturing Process | 97 |
| 3.9-1 | Raw Residual Loads Associated with Continuous Casting | 106 |
| 3.10-1 | Shipments of Steel Products - 1974 (All Grades, including Carbon, Alloy and Stainless) | 111 |
| 3.10-2 | Residues Collected in Rolling Air Pollution Control Facilities | 112 |
| 3.10-3 | Waste Process Water Treatments for Hot Rolling Operations | 113 |
| 3.10-4 | Chemical Analyses of Steel Conditioning Residues | 116-117 |
| 3.10-5 | Scale Collection and Disposition | 118 |
| 3.10-6a | Iron and Oil Content of Rolling Mill Scales | 119 |
| 3.10-6b | Chemical Analyses of Rolling Mill Scales (from the Literature) | 120 |
| 3.10-7 | Chemical Analyses of Hot Rolling Mill Sludges | 121 |
| 3.10-8 | Quantities of Rolling Mill Sludges Generated and their Disposal | 122 |
| 3.10-9 | Quantities of Residues Generated in Rolling Operations by Countries | 123 |
| 3.10-10 | Raw Residual Loads Associated with the Hot Rolling and Cold Finishing Operations | 125 |
| 3.11-1 | Acids Used and Methods of Spent Liquor Disposal | 129 |
| 3.11-2 | Disposition of Waste Pickling Rinse Waters | 129 |
| 3.11-3 | Chemical Analyses of Pickle Sludge | 130 |
| 3.13-1 | Chemical Analyses of Fly Ashes from Southwestern Pennsylvania Area | 137 |
| 3.13-2 | Chemical Analyses of Lime and Limestone FGD Sludges | 138 |
| 3.14-1 | Chemistries of Waste Water Treatment Plant Sludges | 142 |
| 3.14-2 | Quantities and Disposition of Waste Water Treatment Plant Sludges | 143 |
| 3.15-1 | Miscellaneous Facilities Associated Regularly (or Occasionally) with Iron and Steel Mill Operations | 153 |

Chapter Page

3.16-1 Estimates of Iron and Steel Industry Pollution Control Residues in the U.S. in 1974 and Comparison of % of Residues Recycled in the U.S. and Abroad 157

3.16-2 Relative Quantities of Residues Recycled, Sold, "Stored" and Dumped in the U.S. 158

3.16-3 Methods of Beneficiation of Iron and Steel Mill Environmental Pollution Control Residues 161

3.16-4 Chemical Composition of Waelz Oxides 164

# CONVERSION FACTORS AND ABBREVIATIONS

## Conversion Factors

1 kg (kilogram) = 2.2 pounds
1 t (metric ton) = 1.1 short ton
1 m (meter) = 3.3 feet
1 m$^3$ (cubic meter) = 35.3 cubic feet
1 l (liter) = 0.26 gallon

## Abbreviations

AISI = American Iron and Steel Institute
BF = Blast furnace
BOF = Basic oxygen furnace
BSC = British Steel Corporation
CC = Continuous casting
EAF = Electric arc furnace
ESP = Electrostatic precipitator
FGD = Flue gas desulfurization
JISF = Japan Iron and Steel Federation
NA = Not available
OECD, ED = Organization for Economic Cooperation and Development, Environment Directorate
OH = Open hearth
VDEh = Verein Deutcher Eisenhuttenleute (Germany)

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# CHAPTER I CONCLUSIONS AND RECOMMENDATIONS

## 1.1 CONCLUSIONS

The Federal Water Pollution Control Act, the Clean Air Act, their amendments and the regulations for their implementation, are aimed at providing an effective program to improve the quality of the nation's water and air. Due to these strict pollution control laws and regulations, including pollutant discharge limitations, large quantities of dusts and sludges are generated during the removal of the pollutants from the air, off-gases, industrial and process waters. These dusts and sludges are often called pollution control residues or simply residues.

The management and disposal of these residues have created new pollution problems. Their large quantities, their pollution-prone consistencies (fine dusts or dried sludges can dust when exposed to winds) and their land, water (run-off) and ground-water-polluting potentials concern both industry and the government.

The many pollution control facilities in the U.S. steel industry generate a total of more than 16 million tons of residues/year. As shown in this study, more than 100,000 tons/year of residues (dusts and sludges - dry basis) are generated in each of ten subcategories or operations. From raw material processing to finishing operations, the quantities arising/year in million tons in the subcategories are: coking - 1.0; sintering - 0.9; blast furnace (BF) - 3.3; basic oxygen furnace (BOF) - 1.7; open hearth furnace (OH) - 0.5; electric arc furnace (EAF) - 0.4; continuous casting (CC) - 0.2; rolling - 7.4, and pickling - 0.4. In addition, large quantities of sludges (0.7 million tons) are also generated in the joint waste water treatment plants in which effluents from two or more of the above-mentioned primary and, in some cases, secondary water treatment operations are further processed (see Chapter II, Table 8).

The residues are either (1) recycled (or sold), or (2) "stored" for future recycling, or (3) dumped, or (4) sometimes used for a useful purpose. There is also another way to "dispose" of the residues, and that is to eliminate their generation by converting the wastes to commercial by-products.

Presently, approximately 60% of the iron and steel mill pollution control residues are recycled in the U.S. Essentially 100% of the presently generated coking, sintering and coating residues are recycled. The first two are usually reused in the steel plants while the coating residues are reprocessed by the suppliers of the coating materials. Approximately 80% of the BF, 65% of the rolling, and 50% of the continuous casting residues are also recycled, while only 25% or less are reused from the remaining steel mill operations.

Additional large quantities of residues are presently "stored" for future recycling, awaiting either the development of new technologies capable of recycling them in a technically and economically feasible way, or the construction of new agglomerating facilities capable of handling the quantities of residues generated in pollution control. Almost one-half of the presently not-recycled residues are "stored" for this reason. The other half of the not-recycled residues are dumped. For dumping, well-defined areas, not normally accessible to the public, are used. Ravines, valleys, often closed with earth dikes or small dams, are commonly used as dumping sites. Occasionally the dumping areas are lined with clay or tar to avoid ground water contamination.

The residues and wastes are sometimes also used for some practical purposes. For instance, waste pickling liquor for municipal water treatment or for neutralization of alkaline wastes; or dirty waste oils, and scum and tar for dust control on temporary roads. However, the quantities directed to such purposes are quite small.

The regeneration of hydrochloric acid or recovery of sulfuric acid are good examples of processes that eliminate troublesome wastes. Here, instead of generating neutralization sludges (usually hard to recycle or dispose of), commercial by-products are manufactured. Therefore, the problem of residue management and disposal is automatically solved.

To eliminate the possibility of secondary pollution from the dumped pollution control residues and also to conserve mineral resources, the recovery of iron and other non-ferrous values such as zinc, lead, carbon, oil, acids, etc., by recycling the residues is the best approach in managing and disposing of the iron and steel works pollution control residues. In most cases, the U.S. iron and steel industry is moving in this direction, as demonstrated by the fact that approximately 60% of the residues are already recycled and another 20% are "stored" (for future reuse).

The problem of not recycling the residues originates not only from the technical difficulties in handling some of the residues, as pointed out in Section 3.16, Recycling, but also from the following facts:

1) Thus far, there is no single process available for recycling or pre-treating all residues, as a mixture or in subsequent operations, using the same facility.
2) Some of the new processes (e.g., used for recycling of the large quantities of zinc and lead or oil-containing residues) are not yet generally accepted as technically and economically feasible technologies.
3) Most of the U.S. steel corporations do not produce large enough quantities of residues (requiring special processes for recycling or pre-treatment) in one location, to make investment in such facilities feasible.
4) The large capital outlays needed to build these (in some cases, still experimental) facilities is not easily available to the steel companies, and

5) The uncertainty about future regulations affecting the disposal and/or recycling of the residues make the investment in recycling operations risky.

## 1.2 RECOMMENDATIONS

Based on the conclusions of our study and the data and information obtained in England, Germany and Japan, the recommendations described in the following paragraphs can be made:

The U.S. EPA ORD should continue the work on the management and disposal of residues from the environmental control facilities of the iron and steel industry. The work should be concentrated on and high priority should be given to the recycling of (a) zinc and lead-containing iron and steelmaking dusts and sludges, and (b) oil-containing sludges.

In the area of zinc and lead-containing sludges, a technical and economic feasibility study should be commissioned (Phase I) to establish the optimum conditions for recycling of these wastes. As a part of this effort, the use of small installations serving individual mills vs. regional installations serving several steel mills in the same area, should be evaluated. The study should also include a comparison of the advantages and disadvantages of the various available methods with specific coverage of the SL/RN, the Berzelius (Waelz) and the Kawasaki processes.

As a part or a continuation of this study, a demonstration project or projects should be initiated (Phase II) using existing facilities (U.S. or foreign). In this project, several presently not-recycled, typical, zinc and lead (and other tramp element) containing residues from various U.S. steel mills should be treated or pre-treated, to make them suitable for recycling in iron and/or steelmaking operations. The recovery of zinc and lead in these processes would also be evaluated because the economic feasibility of these operations seems to depend on the possibility of also recycling the zinc and lead.

Depending on the findings of the Phase I study, the construction of a U.S. plant for the recycling of zinc and lead-containing residues as an alternative to or a follow-up of the Phase II demonstration project could be considered. This plant, supported with EPA and other funds, would serve as a full-scale demonstration operation. It could be a small facility serving only one mill or it might be a larger regional residue treatment-recycling installation.

To study the recycling of the oil-containing wastes, the U.S. EPA ORD effort should be directed toward:

1) The separation of oils from the effluents before the residues are generated or removed for disposal or recycling, and
2) The separation of oil from the residues in a pre-treatment step before the agglomeration and recycling of the residues.

Again, the commissioning of a feasibility evaluation by the U.S. EPA ORD can be recommended as Phase I. Such a study should determine the technical and economical merits of recycling oily wastes (including the oil recovery aspects of such processes). The evaluation of various already-used oil (physical, physicochemical, solvent extraction and chemical, including emulsified oil-water and oil-sludge) separation systems should be included in such a study. This approach (Phase I) should lead to demonstration projects after the selection of the best processes (Phase II).

*********************

The support of such projects by the U.S. EPA ORD would help the industry to decide on the selection of the most suitable systems for their specific requirements for the recycling of presently "stored" or not-recycled tramp element or oil-containing residues. At the same time, the study and demonstration projects would help the U.S. EPA ORD and the state and local environmental authorities to demonstrate that economically and technically feasible processes are available for the recycling of even those presently not-recycled steel mill residues.

We estimate that of the presently dumped or "stored" 7 million tons of steel mill residues per year, close to 90% (or more than 6 million tons) would be recycled if the availability of technically and economically feasible processes for the recycling of residues can be demonstrated to the steel industry. Even for the industry, the economically feasible recycling of residues is the most attractive solution to the management and disposal of pollution control residues, if the capital can be made available to build such facilities.

For the residues which cannot be recycled as waste, or which are generated during the recycling processes as final wastes, residue stabilization methods should be developed to make the environmentally safe disposal of these residues possible.

# CHAPTER II - INTRODUCTION

## 2.1 PURPOSE

The implementation of the Federal Clean Air Act and the Federal Water Pollution Control Act, and especially their major amendments (the Federal Water Pollution Control Act Amendments of 1972, and the Clean Air Amendments of 1970) resulted in the removal of various pollutants from the air and water.

Because of this effective program to improve the quality of our nation's air and water, large quantities of pollution abatement residues (residues) are generated in the pollution control facilities of the iron and steel industry. The handling and disposal of these residues present new environmental problems.

The purpose of this U.S. EPA Grant R-803619 was to establish (1) in what subcategories of the United States iron and steel industry residues are arising; (2) in what general types of pollution control facilities the residues are generated; (3) in what quantities the residues are collected; (4) what are the chemical composition and main physical characteristics of the residues; (5) how the residues are managed and disposed of, and (6) what the trends are in the management and disposal of these residues.

It was also the purpose of this study to determine the differences, if any, in the above-mentioned areas (1-6) between the steel works of this country and those of other major steel producing nations.

Special attention was to be given to the recycling of the residues, their useful application or potential uses, including resource recovery of metallic and other components such as acids and oils, and to the problems which may make their recycling or useful application impractical.

Finally, it was also the purpose of this study to make recommendations, based on our findings, to the U.S. EPA for future research and demonstration projects which might help to solve the problems of disposal of the generated residues. The research and demonstration projects would, hopefully, lead to resource recovery, reuse, or at least to the stabilization and environmentally safe disposal of the residues, dusts, sludges and other final wastes originating from iron and steelmaking operations.

## 2.2 ORGANIZATION OF REPORT

The conclusions of our study and the recommendations for further research and demonstration projects are described in Chapter I.

This introduction, Chapter II, describes the approaches used to develop the information, the statistical data, and a general description of the United States iron and steel industry as a whole. This is followed by the rationale used for the categorization and subcategorization of the industry, and a general description of the types and quantities of residues generated in the various subcategories.

In Chapter III (Pollution Abatement Categorization by Subcategories) essentially the same approach is used to describe and discuss in detail each of the 14 subcategories: coking; sintering; blast furnace (iron); blast furnace (ferro-manganese); basic oxygen furnace; open hearth furnace; electric arc furnace; vacuum degassing; continuous casting; rolling operations; pickling operations; coating operations; waste water treatment operations, and boilerhouse.

First, the purpose of the iron or steelmaking operations covered in the subcategory is described: what products, from what raw materials, in what type of facilities and in what quantities they are manufactured. The second part contains the description of the types of pollution control facilities used, the types of residues generated, their chemical and physical properties, and the quantities expressed as kg/ton of product generated. To present the data, whenever reasonable, tables are used and in them the data obtained from the literature are also included.

This is followed by a review of the methods used for the disposal of the residues, including estimates on the percent reused, sold or "stored" for future recovery and dumped.

Finally, the information and data obtained on U.S. practices are compared with those of other major steel-producing countries.

## 2.3 METHODS USED TO DEVELOP INFORMATION

We asked the American Iron and Steel Institute (AISI) for help and guidance in obtaining the necessary information on the types, quantities, properties, management and disposal of residues generated in the United States iron and steel industry. After meetings with the representatives of the AISI, the Technical Committee on Environmental Quality Control of the AISI advised us that they had approved a procedure for us to follow in connection with our subject study.

The AISI assured the cooperation of eight of the nine largest U.S. steel producers with a total raw steel production of 105.7 million tons in 1974. This cooperation allowed the authors, in the company of a representative from the AISI Technical Committee on Environmental Quality Control, to visit 11 integrated steel works, having a total of about 35.1 million tons of raw steel production in 1974. They also made arrangements to obtain samples and some data from two additional works having an output of roughly 5.3 million tons.

Based on the fact that raw steel production in the United States during 1974 was 145.72 million tons(1), it can be stated that companies representing about 73% of the United States steel production cooperated through the AISI in our study. The production of the 11 works visited represents 24% and the 13 works from which samples were obtained, 28%, of the total raw steel produced in 1974 in the U.S. The AISI was of the opinion that the plants visited were representative of the U.S. steel industry, and further visits or samplings would not significantly alter the results of our study.

After the preliminary arrangements were made for the plant visit, each company received a detailed questionnaire (of 18 pages), with a covering letter explaining the purpose of the study. The companies were asked to fill out the questionnaires before the plant visits and have them available to facilitate our work during the visits. However, not all companies complied and, in some cases, a considerable period after the visit elapsed before we got the completed questionnaire.

Each plant visit started out with an introduction by the representative of the AISI explaining the reasons for their cooperation. This was followed by a general review of the purpose of our visit. Subsequently, using the completed questionnaire when possible, the various operations (subcategories) of the works were reviewed and production figures checked. The pollution control facilities described and the types and quantities of residues generated in the various pollution control and waste treatment facilities were discussed, along with the fate (reuse or disposal) of the residues.

The second part of the plant visit was a tour of the pollution control facilities of the works during which the operation and performance of the facilities and the generation of the residues was explained and disposal sites visited. After the plant visit, a final question-and-answer period followed, in which the data and information collected during the visit was reviewed. When necessary, additional information and/or samples were requested.

After each plant visit, a trip report was issued and sent to the steel company for approval. The steel companies reviewed the information and data we collected and approved our report, usually with no or only minor changes. Subsequently, the data and information were reorganized and used in the appropriate subcategory (chapter) of our study.

In connection with our study, more than 200 residue samples were analyzed. The samples included iron and steelmaking dusts and sludges, coking, sintering, steel processing (including rolling, pickling, coating), power plant and waste water treatment dusts and sludges. Simultaneously, a literature search was made during which more than 500 articles on the subject matter were reviewed.

The British Steel Corporation (BSC), the Verein Deutscher Eisenhuttenleute (VDEL), and The Japan Iron and Steel Federation (JISF) were contacted and offered cooperation in obtaining information on the arising, management and disposal of residues generated in the pollution control facilities of the British, German and Japanese steel industry. As a result of this cooperation, two steel works were visited in England, five in Germany, and three in Japan, with a total annual production of 5, 11 and 40 million tons in the 2, 5 and 3 steel works, respectively.

In addition to the foreign plant visits, a meeting was held with the In-Plant Fines Group of the BSC and two meetings in Germany with the environmental specialists of the VDEL, the Wirschaftsvereinigung Eisen-und Stahlindustrie and the German government. In Japan one meeting was held with the JISF Committee on Wastes of the Committee on Industrial Location and Environmental Pollution, and one meeting with each of two Japanese government agency representatives (the Environment Agency and the Ministry of International Trade and Industry).

## 2.4 GENERAL DESCRIPTION OF THE U.S. STEEL INDUSTRY

The United States iron and steel industry produced 145,720,000 tons of raw steel in 1974 and 150,799,000 tons in 1973. During the same period the total world production of raw steel was 782,818,000 and 768,570,000 tons, respectively. In other words, the U.S. accounted for 18.6% of the world raw steel production in 1974 and 19.6% in 1973.

Iron and raw steel production figures for the U.S. by steelmaking furnace type for 1973 and 1974 were as follows:

Table 2-1 IRON AND RAW STEEL PRODUCTION IN THE UNITED STATES(1)
(thousands of net tons)

| Year | Iron | Raw Steel | | | |
|---|---|---|---|---|---|
| | Blast Furnace | Basic Oxygen Process | Open Hearth | Electric Arc Furnace | Total |
| 1974 | 95,909 | 81,552 | 35,499 | 28,669 | 145,720 |
| 1973 | 101,208 | 83,260 | 39,780 | 27,759 | 150,799 |

The blast furnace production has increased rather slowly in the last ten years from 88,105,000 tons to 95,909,000 tons in 1974, as can be seen in Table 2-2.

During the same period, however, the open hearth furnace raw steel production decreased significantly from 94,193,000 tons to 35,499,000 tons while the basic oxygen process raw steel production increased from 22.879,000 to 81,552,000 tons and the electric arc furnace production increased from 13,804,000 to 28,669,000 tons (Table 2-3).

In the production of pig and molten iron, various raw materials are used (Table 2-4). Iron ore, including agglomerated iron ore, coke and flux (mainly limestone and dolomite) are the main raw materials needed for iron production, but scrap and other solid wastes such as coarse roll scale and mill cinder are also used as iron-rich raw materials.

The pig and molten iron produced in blast furnaces is used for the production of steels and iron (direct) casting. The other main raw material used in steelmaking is scrap. The consumption of pig iron

Table 2-2 BLAST FURNACE PRODUCTION(1)
(thousands of net tons)

| Year | Basic | Bessemer | Low Phosphorus | Foundry | Malleable | All Other (Silvery Pig Iron, Direct Castings) | Total Iron | Ferro-alloys | Total Blast Furnace Production |
|---|---|---|---|---|---|---|---|---|---|
| 1974 | 91,193 | 1,100 | 106 | 1,528 | 1,382 | 600 | 95,909 | a | 95,909 |
| 1973 | 96,202 | 1,242 | 101 | 1,581 | 1,352 | 359 | 100,837 | 371 | 101,208 |
| 1972 | 83,961 | 1,336 | 105 | 1,977 | 1,193 | 370 | 88,942 | 458 | 89,400 |
| 1971 | 77,341 | 1,215 | 145 | 1,214 | 1,336 | 48 | 81,299 | 393 | 81,692 |
| 1970 | 86,438 | 1,447 | 146 | 1,707 | 1,415 | 282 | 91,435 | 381 | 91,816 |
| 1969 | 89,888 | 1,306 | 96 | 1,850 | 1,456 | 421 | 95,017 | 463 | 95,480 |
| 1968 | 83,396 | 1,437 | 169 | 1,536 | 1,804 | 438 | 88,780 | 553 | 89,333 |
| 1967 | 81,344 | 1,722 | 166 | 1,550 | 1,830 | 372 | 86,984 | 663 | 87,647 |
| 1966 | 83,374 | 2,882 | 209 | 1,673 | 2,848 | 415 | 91,500 | 650 | 92,150 |
| 1965 | 80,431 | 2,716 | 220 | 1,599 | 2,806 | 413 | 88,185 | 674 | 88,859 |

a Included in All Other.

## Table 2-3 RAW STEEL PRODUCTION BY TYPE OF FURNACE(1)
(thousands of net tons)

| Year | Open Hearth[a] | Basic Oxygen Process | Electric Arc Furnace | Total |
|---|---|---|---|---|
| 1974 | 35,499 | 81,552 | 28,669 | 145,720 |
| 1973 | 39,780 | 83,260 | 27,759 | 140,799 |
| 1972 | 34,936 | 74,584 | 23,721 | 133,241 |
| 1971 | 35,559 | 63,943 | 20,941 | 120,443 |
| 1970 | 48,022 | 63,330 | 20,162 | 131,514 |
| 1969 | 60,894 | 60,236 | 20,132 | 131,262 |
| 1968 | 65,836 | 38,812 | 16,814 | 131,462 |
| 1967 | 70,690 | 41,434 | 15,089 | 127,213 |
| 1966 | 85,025 | 33,928 | 14,870 | 134,101 |
| 1965 | 94,193 | 22,879 | 13,804 | 131,462 |

[a] Basic and acid open hearth production.

## Table 2-4 MATERIAL USED BY BLAST FURNACES IN MANUFACTURE OF IRON (PIG AND MOLTEN) IN 1974(1)

| Products | Thousands of Net Tons | Net Tons Per Ton of Iron Produced |
|---|---|---|
| Ore | | |
| Iron ore (incl. manganiferous and block) | 41,163 | 0.429 |
| Manganese ore (incl. ferruginous manganese) | 195 | .002 |
| Agglomerated products (sinter, pellets, etc.) | 116,984[a] | 1.220 |
| TOTAL ores and agglomerated products consumed | 158,342 | 1.651 |
| LESS flue dust and sludge produced | 3,156 | .033 |
| NET - ores & agglomerated products consumed | 155,186 | 1.618 |
| Scrap | | |
| Total scrap consumed | 4,612 | 0.048 |
| LESS produced at blast furnaces & auxiliary units | 1,612 | 0.017 |
| NET - scrap consumed | 3,000 | 0.031 |
| Mill cinder, roll scale, etc. | 4,587 | 0.048 |
| Limestone, dolomite, other flux materials[b] | 23,389 | 0.244 |
| Coke | | |
| Total coke consumed in blast furnaces | 60,606 | 0.632 |
| LESS coke breeze (dust) recovered | 2,165 | 0.023 |
| NET - coke consumed | 58,441 | 0.609 |

a Includes production at or near mine site and at other locations.

b Based on total limestone and dolomite charged directly into blast furnace, plus tonnage consumed in the production of agglomerates.

(including molten iron) and scrap by types of furnaces (e.g., in 1974) was as follows:

Table 2-5 INDUSTRY CONSUMPTION OF SCRAP AND PIG IRON BY TYPES OF FURNACES(1)
(thousands of net tons)

| Year | Type of Furnace | Consumed | | |
|---|---|---|---|---|
| | | Scrap | Pig Iron[a] | Total |
| 1974 | Open hearth | 18,922 | 23,383 | 42,305 |
| | Basic oxygen process | 25,448 | 65,443 | 91,891 |
| | Electric | 28,920 | 1,060 | 29,980 |
| | Cupola | 705 | 263 | 968 |
| | Direct castings | | | 1,877 |
| | Blast | 4,447 | | 4,447 |
| | Other (incl. air furnace) | 696 | 499 | 1,195 |
| | TOTAL | 80,138 | 92,525 | 172,663 |

[a] Excluding molten iron used in direct castings.

(Source: Bureau of Mines)

The steel produced in the various steelmaking facilities may be further treated in vacuum degassing or other refining operations before it is either cast into molds or continuously cast into billets, slabs, etc. The ingots from the molds (after heat treatment in soaking pits) enter the primary rolling mills, where they are converted to blooms, billets or slabs. These blooms, billets and slabs, usually referred to as semi-finished steel, are rolled in hot rolling mills after heat treatment and, if desired, subsequently in cold rolling mills.

A flow sheet (Fig. 2-I) on steelmaking from raw materials to finished mill products shows the main steps in iron-steelmaking and finishing operations, including the most significant coating operations.

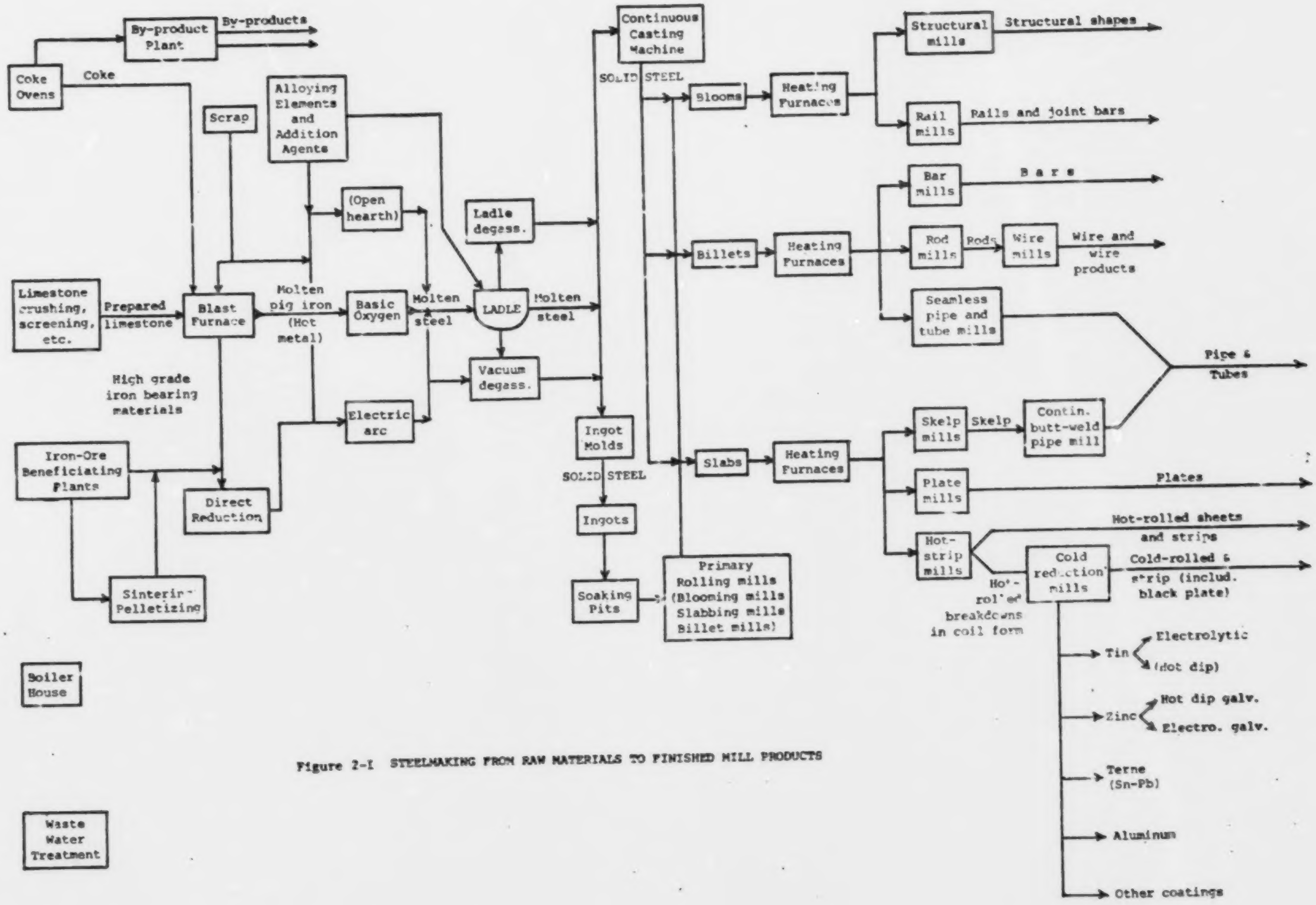
Coke Ovens
Coke
By-product Plant
By-products
Scrap
Alloying Elements and Addition Agents
Limestone crushing, screening, etc.
Prepared limestone
Blast Furnace
Molten pig iron (Hot metal)
High grade iron bearing materials
Iron-Ore Beneficiating Plants
Sintering-Pelletizing
Direct Reduction
(Open hearth)
Basic Oxygen
Electric arc
Molten steel
Ladle degass.
LADLE
Vacuum degass.
Molten steel
Continuous Casting Machine
SOLID STEEL
Ingot Molds
SOLID STEEL
Ingots
Soaking Pits
Primary Rolling mills (Blooming mills Slabbing mills Billet mills)
Blooms
Billets
Slabs
Heating Furnaces
Heating Furnaces
Heating Furnaces
Structural mills
Structural shapes
Rail mills
Rails and joint bars
Bar mills
Bars
Rod mills
Rods
Wire mills
Wire and wire products
Seamless pipe and tube mills
Pipe & Tubes
Skelp mills
Skelp
Contin. butt-weld pipe mill
Plate mills
Plates
Hot-strip mills
Hot-rolled sheets and strips
Hot-rolled breakdowns in coil form
Cold reduction mills
Cold-rolled & strip (includ. black plate)
Tin
Electrolytic
(Hot dip)
Zinc
Hot dip galv.
Electro. galv.
Terne (Sn-Pb)
Aluminum
Other coatings
Boiler House
Waste Water Treatment

Figure 2-I STEELMAKING FROM RAW MATERIALS TO FINISHED MILL PRODUCTS

A general description of various iron and steelmaking operations is given in the introductory part of each chapter dealing with one of the steps of iron and steelmaking.

A detailed, in-depth description of the iron and steelmaking and finishing operations can be found, among others, in "The Making, Shaping and Treating of Steel - Ninth Edition," United States Steel Corporation, 1971(2).

## 2.5 RATIONALE FOR SUBCATEGORIZATION

In the subcategorization of the United States iron and steel industry category, the following were taken into consideration:

A. Prior categorization and subcategorization used in U.S. EPA document(3);

B. Manufacturing processes and products;

C. Standard Industrial Classification (SIC)(4)

D. Size and location of works;

E. Pollution control residue generating facilities, and

F. Quantities of pollution control residues generated.

After all of these factors were considered, we concluded that to include all operations -- found even in complex integrated iron and steel works -- generating significant quantities of pollution abatement residues, the steel industry can be, for the purpose of our study, subcategorized into fifteen (15) subcategories, as described in Table 2-6. The 15 subcategories cover 11 of the 12 subcategories of the EPA document(3). The beehive coke subcategory was omitted because only an insignificant quantity ($<$ 1%) of metallurgical coke is manufactured in beehive coking operations today. The two basic oxygen furnace (BOF) subcategories (semi-wet and wet) and the two electric arc furnace (EAF) (semi-wet and wet) subcategories in the EPA document are discussed in one BOF and one EAF subcategory in our report. However, new subcategories were established based on SIC Group 331 description to include rolling, pickling, coating and waste water treatment operations and the always-present iron and steel mill-related boilerhouse operations. From the SIC Group 331 series, in Industrial No. 3313, only electro-metallurgical steelmaking was included because the only ferro-alloy operation in the U.S. steel mills we visited was a blast furnace-ferromanganese operation, already covered as in the EPA document in a separate subcategory.

Table 2-6 SUBCATEGORIZATION OF THE IRON AND STEEL INDUSTRY

| CATEGORY |
|---|
| 1. Coke-making operations |
| 2. Sintering |
| 3. Blast furnace - iron |
| 4. Blast furnace - ferromanganese |
| 5. Basic oxygen furnace |
| 6. Open hearth |
| 7. Electric arc furnace |
| 8. Vacuum degassing |
| 9. Continuous casting |
| 10. Rolling operations |
| 11. Pickling operations |
| 12. Coating operations |
| 13. Waste water treatment operations |
| 14. Boilerhouse (power plant) |
| 15. Miscellaneous other operations (direct reduction, lime kilns, etc.) |

The 11 plants visited in the United States and the two additional plants from which samples and information were obtained produced the following amounts (thousand net tons) of raw steel in 1974:

810; 857; 1,350; 1,720; 1,820; 2,700; 2,865; 2,920;
3,882; 4,227; 4,430; 4,800, and 8,043.

The locations of the plants are the following:

| | | | |
|---|---|---|---|
| Northeastern | 2 | Middle Atlantic | 4 |
| Northern Great Lakes | 4 | Southern | 2 |
| Western | 1 | | |

The 13 steel plants had the following installations in which pollution control facilities were generating residues:

All plants had rolling pickling and boilerhouse operations; 12 had blast furnaces (iron); 10 had basic oxygen furnaces, coating operations and waste water treatment plants; 9 had coking (by-product); 8 had sintering; 6 had open hearth furnaces; 5 had electric arc furnaces and continuous casting; 3 had vacuum degassing, and 1 had blast furnace (ferromanganese) operations.

During our study it became evident that presently most of the residues generated in the pollution control facilities of the iron and steel industry are arising in eight subcategories: coking, sintering, blast furnace (iron), basic oxygen process, open hearth furnace, electric arc furnace, rolling and pickling. However, to also make our study more comprehensive, six other subcategories were studied and, for the present, even less important residue-generating facilities a "Miscellaneous Other Operations" was established for the purpose of this study.

## 2.6 GENERAL DESCRIPTION OF POLLUTION ABATEMENT RESIDUES GENERATED

In our research, "dry," "wet" and "semi-wet" pollution control residues were considered. "Dry" residues are generated in mechanical collectors (such as primary dust catchers, cyclones, etc.), "baghouses" and dry electrostatic precipitators. "Wet" residues are generated in scrubbers (usually the venturi type), wet electrostatic precipitators, wet cyclones, coarse separators, clarifiers, scale pits, filters (gravity, vacuum or pressure), centrifuges and in various other waste water treatment facilities, including settling ponds.

"Semi-wet" residues are arising when dry residues are wetted (e.g., in pug mills to make the handling of the fine dusts easier) or in drying facilities where most of the water is removed again to make the handling and/or disposal environmentally more attractive.

The consistency of the residues varies from coarse particles (e.g., coarse scale collected in scale pits or iron and steelmaking residues collected in "dust catchers" or "coarse separators") to very fine dusts or fine solid particles in sludges.

Not only the consistency but also the quantities of residues generated can vary even from the same type of iron and steelmaking or finishing operation from mill to mill and even within the same mill from shop to shop, depending on the efficiency of pollutant removal, iron and steelmaking process practice, type and degree of finishing operations, the physical consistency (e.g., hardness and particle size) of the raw materials and the chemical composition of and the ratios of the raw materials used.

The effect of the above variables (even when the pollutant removal efficiency is essentially the same) explains the differences in the quantities of residues generated in the various subcategories of iron and steelmaking, as shown in the following Table 2-7.

In the data, we took into consideration all information obtained from 13 United States, 2 English, 3 Japanese and 4 German integrated steel mills as well as the data obtained from the British Steel Corporation's In-Plant Fines Group, The Japan Iron and Steel Federation, and the Verein Deutscher Eisenhuttenleute (Germany). However, the spread in the quantities of residues generated even in the same country is not significantly smaller(5), as one can see in the tabulations within each subchapter of this report, where not only the management and disposal practices but also the quantities of residues arising are compared.

Table 2-7 QUANTITIES OF POLLUTION CONTROL RESIDUES GENERATED IN VARIOUS IRON AND STEELMAKING OPERATIONS (kg of residue - dry basis - per ton of product)

| Coking |  | Sintering | BF | BOF | OH | EAF | CC | Rolling |
|---|---|---|---|---|---|---|---|---|
| Breeze | Other |  |  |  |  |  |  |  |
| 19-50 | 0.5-1 | 3-33 | 7-55 | 8-35 | 5-20 | 5-20 | 2-25 | 30-102[a] |

BF = blast furnace
BOF = basic oxygen furnace
OH = open hearth furnace
EAF = electric arc furnace
CC = continuous casting
a Per ton of raw steel production

The total quantities of residues generated by the U.S. steel industry's pollution control facilities in 1974 are shown in Table 2-8.

The total quantities of residues generated in the pollution control facilities of the U.S. iron and steel industry were approximately 16.6 million tons (Mt) in 1974. Of this, almost 55%, or 9.1 Mt, was recycled and 45%, or 7.5 Mt, dumped or "stored" for possible later reuse.

The major problem in recycling the presently dumped or "stored" residues is the tramp element content (such as zinc and lead, or oil) of the residues(6). The quantities recycled are discussed by subcategories in Chapter III and in a special Section, 3.16, Recycling.

The cost of pollution control and disposal of the residues generated in the iron and steel industry are not subjects of this study but can be found in government(7,8,9) and other publications(10,11,12).

## Table 2-8 ESTIMATES OF IRON AND STEEL MILL POLLUTION CONTROL RESIDUES IN THE UNITED STATES IN 1974

(million tons/year)

| | Residue Arising | Recycled | Dumped |
|---|---|---|---|
| 1. Coking | 1.0 | 1.0 | < 0.05 |
| 2. Sintering | 0.9 | 0.9 | < 0.05 |
| 3. BF (iron) | 3.3 | 2.3 | 1.00 |
| 4. BF (Fe-Mn) | < 0.05[a] | -[a] | -[a] |
| 5. BOF | 1.7 | 0.4 | 1.3[b] |
| 6. OH | 0.5 | 0.1 | 0.4[b] |
| 7. EAF | 0.4 | 0.05 | 0.4[b] |
| 8. Vacuum degassing | < 0.05[a] | -[a] | -[a] |
| 9. Continuous casting | 0.2 | 0.1 | 0.1 |
| 10. Rolling | 7.4 | 4.2 | 3.2[b] |
| 11. Pickling | 0.4 | - | 0.4[b] |
| 12. Coating | < 0.05 | -[a] | -[a] |
| 13. Waste water plant | 0.7 | - | 0.7[b] |
| 14. Boilerhouse | [c] | [c] | [c] |
| TOTAL | 16.6 | 9.1 | 7.5 |

[a] Insufficient data

[b] Including "stocked" for possible later reuse.

[c] Negligible when low sulfur oil or gas is used.

## 2.7 REFERENCES

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# CHAPTER III - POLLUTION ABATEMENT IN THE IRON AND STEEL INDUSTRY CATEGORY, BY SUBCATEGORIES

The iron and steelmaking process is usually described as consisting of four principal processing steps: (1) preparation of raw materials; (2) raw iron manufacturing; (3) raw steel manufacturing, and (4) finishing of steel products. This is one way in which the iron and steelmaking process can be divided.

For the purposes of this report, however, a subcategorization of the principal processing steps of the iron and steel industry category was necessary. This approach was used not only to follow the previously established subcategorization by EPA but also to more closely identify the arising of the residues generated in the various pollution control facilities. This chapter deals with the 13 principal iron and steelmaking subcategories from coking and sintering to rolling and other finishing operations.

Three more sections or subcategories have been added: one deals with joint waste water treatment plants, another with miscellaneous operations (pig casting, machine and maintenance shops, etc.), and a final section describing the progress and problems in the recycling of pollution abatement residues.

## 3.1 SUBCATEGORY: COKING

Coke, a primary constituent in the blast furnace charge, is the hard, porous aggregate that remains after certain coals are heated to high temperatures in the absence of air. In modern practice, this heating is carried out in long, high but narrow chambers (for example, 3 meters high by 10 meters long by 0.5 meters wide) which are combined in groupings of 50 or more to form a battery. Each chamber is ported at the top to receive the coal charge. Typically, the coal is chuted into the ovens from larry cars which traverse the top of each battery. The ends of each chamber or oven are closed by doors which are removed to facilitate the discharge of the coke at the completion of the carbonization cycle. Subsequently, the coke is quenched.

The ovens are formed of high-grade refractory brick and an intricate arrangement of flues and ducts is built into the walls between chambers, to assure uniform coking of the coal. Heat is supplied to the ovens through these flues and ducts. A regenerative heating system is used and each battery contains its own set of checker chambers which are used for preheating the gases. The coke oven and blast furnace gases are normally utilized as fuel.

Volatile constituents driven from the coal during the roughly 17-hour coking cycle are withdrawn through ducting attached to the top end(s) of the oven chambers. From here the gases and vapors are drawn into a collecting main(s) where spray water (recycled flushing liquor) is used to cool and convey the gases and condensed liquids to a by-product plant where the gas is, in effect, cleaned in preparation for its subsequent use as fuel throughout the plant.

The liquids from coking operations are generally designated as: ammonia liquor, tar and light oil. These primary products are broken down in the secondary operations of the by-product plant into their many components in line with the internal or marketing needs.

In 1974 54,707,597 tons of metallurgical coke was produced by the U.S. iron and steel industry$^{(1)}$.

Almost all integrated steel mills contain by-product coking plants. These operations are a major source of concern with regard to air and water pollution potential. From the coking aspect, the following procedures or phases are recognized as being historically dirty:

A. Charging - The placing of fine coal into hot ovens is the primary source of pollution$^{(2)}$ with the evolution of hydrocarbons, steam, particulates, CO and $H_2S$.

B. Coking or Carbonization - A well-sealed oven will produce few, if any, emissions during this conversion period. However, this depends on good maintenance procedures, particularly with regard to the doors and sealing of the charge ports.

C. Pushing - Emptying of the oven after firing is an inherently dusty operation complicated at times by incomplete coking of the charge. Phenol and cyanide releases are an additional problem$^{(2)}$.

By-product operations are primarily concerned with the conversion of the condensed, and volatile constituents from the coking operation into marketable or useable products. Regardless of the sophistication of this operation, process wastes always remain. These wastes are troublesome from a disposal standpoint and efforts to make them less so results in pollution control residues.

All but 2 of the 11 plants visited for this study had coking facilities. These ranged in size and output from one battery of 75 ovens with a 1974 production of slightly under 400,000 tons to a seven battery, 500+ oven installation with just under 3,000,000 tons for 1974. Five plants reported on their efforts to reduce charging emissions. These included smokeless larry cars on four of 16 batteries at three plants: a stage-charging system on the one battery at one plant; an AISI larry car on one of six batteries at another facility, and a coal preheat and steam charging installation on one of seven batteries at one plant. The waste water effluents from the scrubbers on the smokeless larry cars were, in all cases, discharged to the quench water circuits serving those batteries and neither the quantities nor the chemical composition of these wastes were reported.

The limiting of emissions during carbonization, as previously indicated, depends primarily on good maintenance procedures. In our discussions at the various plants, it was obvious that concerned personnel were well aware of this and efforts were being made in this direction.

Only two batteries (one at each of two plants) are equipped with devices designed specifically to alleviate pushing emissions. One of these is a hood extending the length of the battery. A wet scrubber is provided to clean the exhaust from this hood with a reported collection of 0.12 kg of dry residue/ton of coke. The residue is combined with the sump breeze from the quenching operation. The other collection system consists of a hooded coke car also equipped with a wet scrubber which, again, discharges its liquid wastes to the adjacent quench water circuit. In this instance, exact figures as to the quantity of residue from the push car collector were not available but an increase in sump collection is noted in the following discussion on quench station residues.

The quench water circuits at all of the plants we visited were closed loop with fresh water makeup and a sump to settle out suspended solids. Four plants reported sump breeze collections in the 3.5 kg/ton of fired coke to 9 kg/ton range. The latter figure is for the one battery provided with the push car coke dust collector noted in the above paragraph. The other batteries at the site that do not have charging or pushing pollution control devices are listed as yielding only 5 kg of sump residue per ton of coke. Most of the sump breeze is sold (larger pieces, primarily) and used for soaking pit bottoms or in the sinter mix. Only a small amount was delegated to stock.

Only one plant reported a pollution control residue as the result of their by-product operation. (All of the others considered their plant effluents as process wastes.) This plant had a biological treatment system (see Figure 3.1-I) that yielded 3.8 kg of lime-biomass residue (filter cake - dry basis) per ton of coke. This residue was landfilled. One other plant also had a biological treatment system but it was discharging the liquid effluent from this plant into a nearby stream. Consequently, no residue was reported, per se.

The chemical composition of coke breeze is usually between 80-90% C, with the balance varying with the chemistry of the inorganic components (ash) of the various coals used in the coking operations.

Because the coking pollution control residues are recycled (and, therefore, no problem exists with the management and disposal of these residues) no investigation was made either on the variation in chemistry or in particle size of these residues.

In most coking operations the coke breeze (sometimes called "sump breeze") originating in the coke-quenching operation is mixed with the coke breeze obtained in screening and dedusting operations. The total quantities of coke breeze generated in all of the operations are usually reported by companies and institutions. The quantities of strictly pollution control mixtures are reported in Table 3.1-1 and are compared with the total quantities of coke breeze collected in the coking operations.

The quantity of total coke breeze collected in the U.S. is approximately 36 kg/ton(1) to 57 kg/ton(10) of coke produced. Another respected source(3) gives a range of 50-100 kg/ton of coke produced. Since total coke breeze figures are usually given in England(4), Germany(5) and Japan(6) as well as in the U.S., and because various size fractions (including the pollution control residues) may be included or excluded in the coke breeze figures, a direct comparison is not possible.

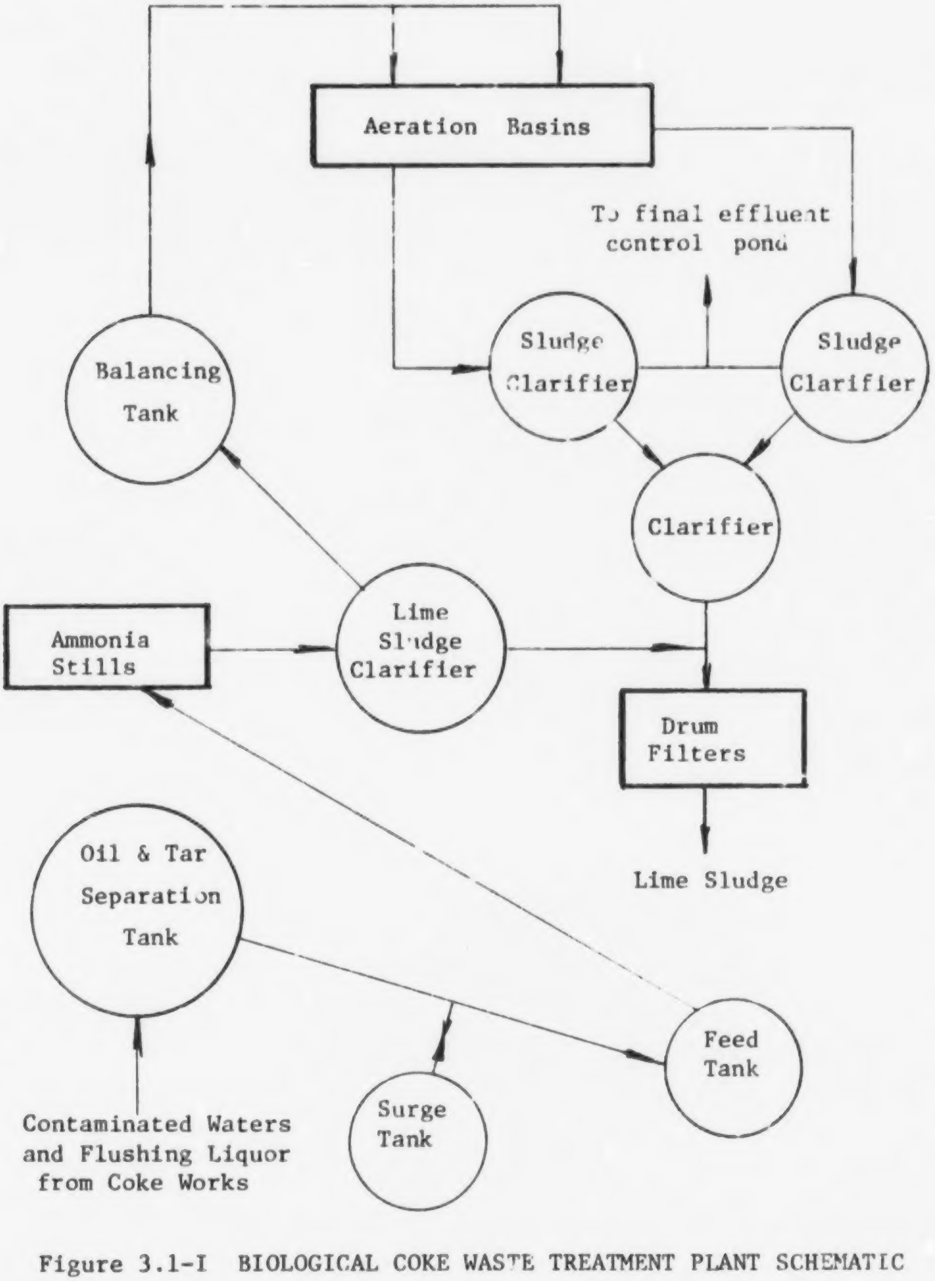
Aeration Basins
To final effluent control pond
Balancing Tank
Sludge Clarifier
Sludge Clarifier
Clarifier
Lime Sludge Clarifier
Ammonia Stills
Drum Filters
Lime Sludge
Oil & Tar Separation Tank
Feed Tank
Surge Tank
Contaminated Waters and Flushing Liquor from Coke Works

Figure 3.1-I BIOLOGICAL COKE WASTE TREATMENT PLANT SCHEMATIC

Therefore, the figures have to be looked at, taking this loose definition of coke breeze into consideration.

Table 3.1-1 QUANTITIES OF COKE BREEZE AND COKING POLLUTION CONTROL RESIDUES GENERATED IN STEEL MILLS
(kg/ton of coke produced)

| | Total[b] | Strictly Pollution Control Residues[a] |
|---|---|---|
| United States | 36(1) | 3.5 - 9 |
| England | 30 - 40(4) | 1.7 - 8 |
| Germany | 25 - 40(5) | NA |
| Japan | — | 10 - 20(6) |

a Includes unloading, charging, coking cycle, discharge and quenching.

b Includes screening coke breeze and pollution control residues.

The OECD, ED reported(7) all the airborne and waterborne residues generated in coke operations based on information supplied by six European countries and the U.S., Japan and Canada (Table 3.1-2).

The pollution control facilities on the coking operations are essentially the same in Europe and Japan as in the U.S. For the dedusting during the charging and coke-pushing cycles, only experimental setups are in operation; however, everywhere (as it is in the U.S.) the trend is toward dedusting of these operations. The clarification and recovery of coke breeze from the quenching waters is also similar. The coke breeze and the residues are recycled mostly through the sintering operation although in some cases, it is returned to the coal piles, used in soaking pit bottoms, or, occasionally, briquetted and used for various purposes.

The only major difference in the pollution control and residue generation of the coking operations is the trend towards complete control of the $SO_2$ or $H_2S$ emissions in Japan. All three huge integrated steel mills we visited in Japan had coking off-gas desulfurization units. All of these operations, however, convert the sulfur in the off-gases to commercial elemental sulfur, ammonium sulfate, gypsum or sulfuric acid, in place of producing residues. The processes used in these desulfurization operations are the Diamox (developed by Mitsubishi Chemical Industries, Ltd.), the Ammonia Takahax Wet Oxidation method (by Nippon Steel Chemical Company), and the Fumax process (by Sumimoto Chemical Engineering Company). In the U.S. (while not generally accepted yet) the Karl Still, Koppers,Claus and other processes are used for the same purpose. These are similar to or the same processes also used in Europe.

## Table 3.1-2 RAW RESIDUAL LOADS ASSOCIATED WITH COKE MANUFACTURING OPERATIONS(7)

| Type of Discharge | Raw Residual Load kg/ton of coke |
|---|---|
| Airborne residuals | |
| Particulates | 30.0 - 50.0 |
| Sulfur dioxide | 0.2 - 1.0 |
| Hydrocarbons (tar) | 4.0 - 8.0 |
| Hydrogen sulphide | 0.1 - 0.8 |
| Hydrogen cyanide | 0.1 - 0.6 |
| Waterborne residuals | |
| (effluent flow, lit./ton) | (730) |
| Ammonia | 1.5 |
| Phenol | 0.3 |
| Cyanide | 0.15 |
| $BOD_5$ | 0.9 |
| Sulphide | 0.3 |
| Oil and grease | 0.09 |
| Suspended solids | 0.07 |
| (pH) | (6 - 9) |

## 3.1 REFERENCES - COKING

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8) Trace Pollutant Emissions from the Processing of Metallic Ores. U.S. Environmental Protection Agency, EPA-6502-74-115, October 1974.

9) Speight, G. E. Best Practical Means in the Iron and Steel Industry. The Chemical Engineer, March 1973, pp. 132-139.

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## 3.2 SUBCATEGORY: SINTERING

Sinter and pellets are major, relatively new industrial constituents in modern blast furnace practice. Both provide iron units and both have improved furnace operations largely because of their closely controlled sizing. The measure of their importance is the fact that almost three times as much agglomerated material (sinter, pellets, etc.) was used for charge material in making iron in 1974 as raw iron ore(1) (approximately 117 million tons of agglomerated products vs. 41 million tons of raw iron ore).

Since pellet production is almost exclusively tied in with mining and ore concentrating operations far removed from basic iron and steelmaking facilities, pellet plants did not fall within the scope of this study. Sintering, on the other hand, is principally an integral or closely associated steel plant operation since many of the base materials for sinter are found in the integrated steel mills.

Sinter is a hard, porous agglomerate formed by fusing a wide variety of fines together on what is known as a sinter machine or strand. The raw sinter mix can vary considerably but may typically include naturally fine ore, iron concentrates, ore fines from screening operations, BF flue dust and sludge as well as other iron-bearing residues from plant operations. The addition of BF fluxing agents, to make "fluxed" sinter, is becoming increasingly popular. These materials are blended with a fuel (coke breeze or coal fines) and return sinter fines in a mixing drum or disc. The latter results in the "granulation" of the mix so that the feed to the sinter machine consists of a wide range of odd-sized and shaped granules resulting in the formation of a permeable bed.

The sinter machine itself is, in effect, an endless moving belt with the conditioned mix placed on the feed end and the finished hot sinter coming off the opposite or discharge end. The belt consists of a large number of pallets containing high temperature grates which support the bed. Rolls on the sides of these pallets ride on side rails and permit the pallets to be pushed along. A firing hood on the head end of the machine ignites the fuel in the top of the bed and air is drawn through the material and grates as the pallets move slowly down the machine. With a properly proportioned fuel addition, the flame front developed from the ignited firing progresses down through the bed. When this front reaches the bottom of the material, the finished sinter is ready for discharge. In the latest machines, a thin hearth layer of fired sinter is deposited on the grates prior to the raw sinter mix. This serves to lower grate temperatures and prevent damage to the grate bars at burn-through.

Temperatures developed during sinter firing are such that fusion of the bed takes place and large, porous sintered masses are formed. These masses are given an initial crushing and sizing as they leave the machine. The still-hot sinter then goes to a cooling station and then to additional crushing and screening operations to yield the final sized product. Forced air coolers are normally used although water quenching was employed at two of the plants we visited.

Sinter machines vary widely in size and capacity. With the recent adoption of higher suction (increased air flows and pressure drops across the bed) the capacity of the machines expressed as sinter output per square foot of grate area per unit of time continues to increase. This, combined with technological advances in grate and machine design, has resulted in single strands with a rated annual output of over 4,000,000 tons of sinter per year in contrast to earlier strand ratings of 500,000 tons per year or less.

The seven plants we visited with sintering operations contained a total of 17 strands with variations of from one to six machines per plant. 1974 sinter production from these facilities was a total of 12,000,000 tons and ran from slightly more than 500,000 tons at two of the plants to roughly 2,500,000 tons at one plant. Total industry-wide production for the year was 40,769,185 tons (including some briquettes and nodules)(1).

Sinter operations are inherently dusty. Particulates, as well as combustion products, become entrained in the gas stream (windbox exhaust) as it is drawn through the sinter bed and substantial quantities of airborne dust are generated from the cooling, screening and sizing of the sinter at the discharge end of the machine. In the more recent sinter plant installations and those older plants where pollution abatement equipment have been added, both wet and dry collection systems are used to clean the windbox exhaust in addition to the basic primary mechanical collectors with which these machines are equipped. Venturi scrubbers are the choice for the wet systems and either electrostatic precipitators or baghouses for the dry. Where collection equipment is used on the discharge end operations, dry collectors are the usual choice including high efficiency cyclones and baghouses.

The following tables outline our findings in those plants we visited with regard to the collection equipment they use:

"Windbox" Exhaust Control

| | No. of Plants |
|---|---|
| Dry ESP | 2 |
| Mechanical only | 2 |
| Baghouse | 1 |
| Scrubber | 1 |
| Dry ESP & scrubber | 1 |

"Discharge End" Emission Control

| | No. of Plants |
|---|---|
| Mechanical | 2 |
| Baghouses | 2 |
| Scrubbers | 1 |
| Water quench | 2 |

The water circuit for the one windbox exhaust gas scrubber shown above is closed loop with a bleed to a secondary treatment system. The discharge end scrubber water is once-through with pariculate removed in a joint treatment facility. In the two water quench application, the water used to quench the hot sinter (rather than air or forced draft cooling) is recycled with a blowdown to settling ponds for sludge removal. One of these two plants also has a mechanical collector on the discharge end of one of their four sinter machines.

We were not able to obtain as much factual information on the quantity and nature of sinter plant emissions from our plant visits as we would have liked, because virtually all of the collected dusts and sludges are recycled directly to the sinter strand, usually without weighing or chemical analysis. Since the sintering operation includes a built-in recycle system (for hot and cold return fines), the recycling of these emission control residues poses no major problem. The data we were able to develop with regard to the chemical makeup of the collected residues of the plants is given in Tables 3.2-1 and 3.2-2. With the exception of the high alkali content in the windbox dust from plant G there are no indicated chemical reasons why recycling is not practical. Plant G does, however, landfill their windbox dust for the afore-mentioned reason.

Table 3.2-3 lists the chemical analyses of sinter dust as reported by several literature sources. Table 3.2-4 gives sizing data on our samples indicating great variation in the size of the particles of the sintering residues. Data obtained from the literature indicate the same variation in particle mix distribution. A British source(5) reports similar data as our Plant E for ESP dust (i.e., 19-41%) while others report 61%(2), 84%(4) and 98.1%(3) in the -325 mesh range.

The reason for the little substantive data gathered on the quantities of dusts and sludges generated at these plants is that these residues have almost without exception been successfully absorbed into the sinter process and are no longer considered as troublesome wastes. Consequently, the pollution control personnel we had contact with had little knowledge,or real concern with, specifics on this

Table 3.2-1 ANALYSIS OF SINTERING "WINDBOX" END POLLUTION

CONTROL RESIDUES
(% dry basis)

| Plant | Sample | Total Fe | C | Zn | Pb | $K_2O$ | $Al_2O_3$ | Sn | $SiO_2$ | CaO | MgO | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Sludge 1 | 57.0 | 5.4 | 0.02 | 0.04 | 0.17 | 2.4 | 0.04 | 5.2 | 0.21 | 0.15 | 0.16 |
|  | Sludge 2 | 51.5 | 13.6 | 0.02 | 0.06 | 0.27 | 2.1 | 0.01 | 4.7 | 0.12 | 0.09 | 0.27 |
| D[a] | Sludge | 20.3 | NA | NA | NA | NA | 3.0 | NA | 19.0 | 22.0 | 11.0 |  |
| E | Dust 1[a] | 52.9 | 7.9 | 0.02 | 0.04 | 0.57 | 1.7 | 0.02 | 5.3 | 4.3 | 2.0 | 0.29 |
|  | Dust 2[b] | 50.1 | 6.1 | 0.01 | 0.02 | 0.36 | 1.5 | 0.02 | 5.2 | 5.3 | 2.7 | 0.19 |
| G | Dust[d] | 22.5 |  |  |  | 10.4 | 1.04 |  |  | 16.2 | 4.6 | 1.2 |
| I | Sludge[c] | 34.1 | 6.6 |  |  | 3.8 | 5.9 |  |  | 12.3 | 3.0 | 0.7 |

a Results obtained from the steel company

b Electrostatic Precipitator dust

c Contained also 1 - 2% oil

d Contained also 0.36% oil

## Table 3.2-2 ANALYSIS OF SINTERING "DISCHARGE" AND POLLUTION

CONTROL RESIDUES
(% dry basis)

| Plants | Sample | Total Fe | C | Zn | Pb | $K_2O$ | $Al_2O_3$ | Sn | $SiO_2$ | CaO | MgO |
|---|---|---|---|---|---|---|---|---|---|---|---|
| D[a] | | 21.7 | Na | NA | NA | NA | NA | NA | 10.0 | 31.0 | 30.0 |
| E | Sludge[b] 1 | 23.2 | 8.0 | 0.01 | 0.01 | 0.23 | 1.6 | 1.7 | 5.9 | 27.4 | 2.6 |
| | Sludge[b] 2 | 37.5 | 8.6 | 0.01 | 0.02 | 0.29 | 2.8 | 0.04 | 6.5 | 13.8 | 2.0 |
| C[a] | Dust[c] 1 | 18.4 | NA | NA | NA | NA | 1.2 | NA | 6.20 | 30.4 | 15.7 |
| | Dust[c] 2 | 18.4 | NA | NA | NA | NA | 1.2 | NA | 5.85 | 30.2 | 14.5 |
| | Dust[c] 3 | 18.5 | NA | NA | NA | NA | 1.35 | NA | 5.96 | 29.7 | 14.9 |

[a] Results obtained from the steel company

[b] From hot quench operation

[c] Baghouse dust

Table 3.2-3 ANALYSIS OF SINTER PLANT DUST (FROM LITERATURE)
(% dry basis)

| Ref. | Tot.Fe | C | Zn | Pb | $K_2O$ | $Al_2O_3$ | $SiO_2$ | CaO | MgO | S | $TiO_2$ | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 43.5 | 3.2 | 0.03 | NA | NA | 3.5 | 8.6 | 15.5 | 1.5 | 0.2 | 0.7 | NA |
| 3 | 45.0 | .8-5 | 0-3 | 0-.05 | NA | 1.9--3.8 | NA | 5.6--7.0 | NA | 3-4 | NA | 0-7 |
| 4 | 45.3 | 3.2 | 0.15 | 0.05 | NA | 3.2 | 9.3 | 7.9 | 0.7 | 0.6 | 0.5 | NA |

### Table 3.2-4 PARTICLE SIZE ANALYSES OF SINTER PLANT RESIDUES

(Cumulative Percent Retained on Screen)

| | Plant A[a] | | Plant E | | | |
|---|---|---|---|---|---|---|
| | Windbox Scrubber Sludge | | ESP Dust | | Cooling Water Sludge[b] | |
| Screen | Sample 1 | Sample 2 | Sample 1 | Sample 2 | Sample 1 | Sample 2 |
| 8 mesh | - | - | - | 0.2% | - | - |
| 16 mesh | - | - | 0.7% | 2.5 | - | - |
| 30 mesh | - | 0.1% | 2.8 | 13.0 | - | - |
| 50 mesh | T | 0.5 | 8.1 | 24.7 | - | - |
| 100 mesh | 1.5% | 5.5 | 21.5 | 40.2 | - | - |
| 200 mesh | 18.4 | 25.7 | 43.8 | 64.6 | - | - |
| 325 mesh | 37.3 | 42.0 | 60.4 | 79.7 | - | - |
| 325 mesh[c] | 27.5 | 25.5 | 59.4 | 81.4 | 3.4% | 1.9% |
| 20 micron | 52.6 | 48.4 | 79.1 | - | 22.7 | 17.7 |
| 10 micron | 64.1 | 61.2 | 84.3 | - | 44.6 | 39.1 |

[a] Plant A secured this sample from their companion operation.

[b] Settled sludge from blowdown of closed loop water cooling circuit.

[c] Separate screening of another portion of sample.

material. The information we were able to gather as to types, quantities and dispostion are in Table 3.2-5.

An EPA(8) source gives a dust output for sintering operations as about 21 kg/ton. In the U. S. plants which we visited 3-25 kg of sinter residues are generated/ton of sinter produced; in European plants 15-30 (in England 19(5), in Germany 15-30) and in Japan, 13-20 kg were reported. The OECD, ED report(7) estimates the airborne residues to be between 15-25 kg/ton and the suspended solids 8.3 kg/ton (Table 3.2-6).

As in the U.S., the sintering pollution control residues are also recycled in Europe and in Japan. However, in Europe and in Japan when the Zn and Pb content of the residues is getting high due to Zn and Pb accumulation, the residues are recycled through special processes such as the SL/RN or Waelz processes. In these processes, the Zn and Pb are volatilization-separated from the iron-rich matrix at elevated temperatures in a reducing atmosphere. Subsequently the Zn and Pb is recovered from the separated Zn and Pb-rich residues. For details on these recovery processes, see Section 3.16, Recycling.

In two mills of the three we visited in Japan, $SO_2$ as well as particulate matter is removed from the sinter off-gases. At one of the plants the end product of the desulfurization on two sintering units is high-purity gypsum. At another plant (on one unit) the end products of desulfurization are either ammonium sulfate crystals or gypsum, both regarded as high-quality saleable commercial by-products.

While the quantities of these by-products vary depending on the sulfur content of the sintered materials, they are not regarded as pollution control residues since they are sold as commercially valuable products.

Table 3.2-5 TYPES AND QUANTITIES OF RESIDUES GENERATED IN U.S.

SINTERING OPERATIONS AND THEIR DISPOSAL

| Plant | Residue |  | Residue Quantities |  | Disposition |
|---|---|---|---|---|---|
|  | Dust | Sludge | Dust | Sludge |  |
| I | x | x | NA | NA | Recycle - sinter |
| J | x | Joint | NA | NA | Recycle - sinter |
| G | x | - | 24.5 kg/ton | - | 80% recycle -sinter<br>20% landfill |
| K | x | - | 2.9 kg/ton[a] | - | Recycle - sinter |
| F | x | - | 5 kg/ton | - | Recycle - sinter |
| D | x | - | NA | - | Recycle - sinter |
| E | x | x[b] | 6.2 kg/ton | .95 kg/ton | Dust - sinter<br>Sludge - stock |

[a] Baghouse portion - no figure available on cyclone residue

[b] Sludge from hot quench operation

Table 3.2-6 RAW RESIDUAL LOADS ASSOCIATED WITH SINTER PLANT OPERATIONS (7)

| Type of Discharge | Raw Residual Load (kg/ton of sinter) |
|---|---|
| Airborne residuals | |
| Particulates | 15.0 - 25.0 |
| Sulfur dioxide | 1.0 - 12.0 |
| Waterborne residuals | |
| (Wet particulate control system) | |
| (Effluent flow, lit./ton) | (1,043) |
| Suspended solids | 8.3 |
| Oil and grease | 0.6 |
| Sulphide | 0.2 |
| Fluoride | 0.03 |
| (pH) | (8 - 10) |

## 3.2 REFERENCES - SINTERING

1) Annual Statistical Report for 1974. American Iron and Steel Institute, Washington, D. C., 1975.

2) Saito, Y. Direct Reduction Process for Recycling Steel Plant Waste Fines. In: Proceedings of Ironmaking Conference, Vol. 34, ISS-AIME, Toronto, 1975.

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## 3.3 SUBCATEGORY: BLAST FURNACE (IRON)

The blast furnace (BF), the basic unit for the production of iron, has an evolutionary history dating back some centuries. However, it has only been during the last hundred years that the rapid strides have taken place which make these units the highly efficient mass producers of this essential metal that they are today. In capsule form, the blast furnace reduces an iron-bearing charge to iron and a gangue slag. Coke, as heat source and reducing agent in the charge, air as hot blast, and limestone or dolomite as fluxes, are the essential ingredients which, with time, produce the transformation of the raw materials to iron.

The furnace charge and firing practice vary considerably throughout the industry. The choice of raw materials, their physical and chemical make-up, and the iron grade desired are but a few of the reasons for this. The U.S. steel industry in 1974 (when 95,909,000 tons of iron were produced(1)) consumed the following materials per ton of iron produced in the blast furnaces:

| | |
|---|---|
| Ore and agglomerates | 1.618 tons |
| Scrap | 0.031 tons |
| Flux materials | 0.244 tons |
| Cinder, scale, etc. | 0.048 tons |
| Coke | 0.609 tons |

The ore and agglomerates are the main iron-bearing components. Agglomerates are normally pellet and/or sinter although some nodules and briquettes are also used. Pellets are produced in conjunction with mining and concentrating operations and, like the ores, are shipped to the mill complexes by boat or rail. Sinter, on the other hand, is a product of in-plant or closely associated operations since it is the vehicle by which many of the plant fines and waste residues, including those resulting from pollution abatement procedures, are effectively recycled(2).

The blast furnace is a tall circular refractory-lined steel shell with a working height of up to 30 m (100 ft.) and a hearth diameter on the bottom of from 3-12.2 m (10 to over 30 ft.) in diameter in the U.S. and up to 14.6 m (47.4 ft.) in Japan and Europe.

The charge is inserted at the top of the shell in a rather unique manner which assures the sealing of the furnace and the collection of the off-gases. As the burden moves down the furnace column it is subjected to heat supplied by the burning of the coke in the presence of hot fuel-enriched blast air introduced through a series of tuyeres near the bottom. Carbon monoxide formed by the burning of the coke is the primary reactant reducing the iron ore and, in general, the iron oxides to metallic iron in the charge. The fluxing agents permit the forming of a slag at operating temperatures enabling the gangue (largely silica and alumina) to be effectively carried out of the furnace in a hot and liquid slag form.

Smelting of the charge yields iron and slag which are periodically removed from the bottom of the furnace and a continuous discharge of blast furnace gas out of the top. In the largest furnaces in Japan and Europe, the iron and slag is essentially continously removed.
Most of the iron (about 90%) is retained in liquid form for subsequent refining into steel with a small amount going directly to associated foundaries. The balance is cast into pigs for convenience in handling and later remelting in cupolas or similar furnaces in the casting industry. The hot molten slag is normally solidified with the help of water and combed for entramped residual metal before disposal or reuse. Because of their heating value, the large volumes of blast furnace off-gases are used within the plant as an important fuel.

Blast furnace sizing varies considerably, the more modern units generally being of the larger capacity. The newest and largest furnaces in the U.S. can produce 4,500-8,000 tons of molten iron daily, and at top operating levels can reduce a charge to metal in less than six hours.

The annual capacity of the largest U.S. unit already in operation is approaching 2 million tons; the largest Japanese and European blast furnaces have a 4 million tons/year capacity. Of the plants we visited, the number of furnaces per plant varied from 1 to 8 with a total number of 42, although all of these furnaces were not in operation. The following table gives the range of iron production capabilities for these mills:

| Work's Iron Capacity (million tons/year) | Number of Plants |
|---|---|
| $<0.5$ | None |
| 0.5 - 1.0 | 2 |
| 1.0 - 1.5 | 1 |
| 1.5 - 2.0 | None |
| 2.0 - 3.0 | 4 |
| 3.0 - 4.0 | 1 |
| $>4.0$ | 2 |

The AISI Annual Statistical Report lists 135 of the 197 American furnaces as in blast at the start of 1975(1).

Unlike some of the steel refining steps to follow, BF smelting itself is an inherently non-polluting operation from a particulate standpoint. The furnace is sealed and the top gases are collected for further use as an in-plant fuel or burned before release to the atmosphere. Ahead of the furnace, stacking, blending and materials-handling phases can be and are a source of air contamination, but these discharges are of a comparatively minor nature in the overall picture and most plants make a reasonable effort to control these dusts within the confines of the plant. The same holds true for the periodic tapping and teeming operations when the iron and slag are removed from the furnace. In the long run, however, even these emissions will be better controlled (not so much from the particulate standpoint but rather because of their gaseous constituents which represent possible health hazards to operating personnel), to comply with the air pollution control regulations.

At present, the only pollution abatement residues arising from BF operations are those associated with the cleaning of the off-gases to make them suitable as an in-house fuel. The quantity of these gases is quite significant in that 4,920 pounds (or roughly 63,500 scf(2)) are generated for each ton of molten iron. The cleaned gases, with their high CO content (about 25%) and resultant heat value of 75-90 BTU/ft.$^2$, are used primarily as reheat for the stoves and for a number of other secondary applications within the plant.

The standard industry approach to BF gas cleaning is to use a dual processing procedure. The first or primary phase yields a dry residue while the second (which may vary considerably in sophistication) results in a dust-ladened water slurry. All furnaces are equipped with dust catchers as the primary or dry dust-collecting source. These units are large brick-lined chambers which, by virtue of an increasing volume and reversal in gas stream direction, cause the heavier entrapped particles to settle out. Only one of the plants we visited reported an additional dust source from one bank of furnaces. Here, that portion of the gas intended for boiler firing was passed through multiclones after the dust catchers with no subsequent processing.

The ten plants we visited had a total of twelve BF shops (two plants had two separate BF sections). Eight of these twelve installations used scrubbers (largely venturi) as the wet phase of their dust removal systems. The four other plants utilized wet electrostatic precipitators in conjunction with washers and/or scrubbers for final processing. One of the eight had precipitators in the line but was not using them, and another followed their venturis with disintegrators.

The rather dilute wet cleaning effluents are first sent to thickeners or clarifiers for an intermediate concentration of the solids, and then on to filters or sludge basins for final thickening. Eight plants we observed used vacuum filters and three, sludge basins. At this stage, the sludge or filter cake has a solids content in the 75-80% range at which level it can be reasonably handled by trucking.

Closed loop treatment of the process waters (both cooling and gas cleaning) for blast furnace shops are gaining increasing popularity, with four of the eleven shops now using this approach and several others either in the installation stage or actively considering recycling of water at the time of our visit. All of the closed loop circulating systems utilize a bleed to balance their loops, and all have a cooling tower in the circuit. Chemical additives to facilitate settling or control contaminants are used by one half of the plants, and joint treatment facilities in two cases.

The chemical makeup of the dust and sludge from these pollution abatement procedures can vary widely from plant to plant, and even within a plant with respect to time. Obviously, changes in the chemical composition or physical consistency of the charge materials and their proportions, firing practice and the grade of iron being produced will have an effect on the amount and composition of the entrained solids and gaseous products carried out at the top of the furnace. Tables 3.3-1 lists the results of our chemical analyses of the dust and sludge samples collected for this study.

The main constituents of the blast furnace residues are iron and carbon. The total iron content of the samples we have analyzed varied between 16.8% and 54% while the carbon content varied between 17.3% and 53%. In most cases, the sum of Fe and C was between 50-75%, making the recycling of these residues attractive.

Table 3.3-1 CHEMICAL ANALYSES OF BLAST FURNACE RESIDUES - DUST PART 1
(weight %)

| | Sample | Fe | C | S | Pb | Sn | Zn | Mn | $Na_2O$ | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ | As | Sb | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | 34.4 | 30.4 | 0.28 | 0.01 | 0.01 | 0.09 | 0.15 | 0.05 | 2.4 | 3.2 | 4.6 | 2.8 | 7.6 | <0.02 | <0.01 | <0.01 |
| | 2 | 38.2 | 28.5 | 0.27 | 0.01 | 0.01 | 0.09 | 0.12 | 0.08 | 2.3 | 5.0 | 5.1 | 2.9 | | | | |
| | 3 | 36.2 | 32.4 | 0.14 | 0.01 | 0.02 | 0.09 | 0.06 | 0.07 | 2.7 | 2.0 | 4.2 | 2.2 | | | | |
| | 4 | 31.4 | 31.5 | 0.18 | 0.01 | 0.04 | 0.07 | 0.14 | 0.10 | 4.5 | 3.4 | 5.4 | 3.0 | | | | |
| E | 1 | 31.3 | 36.1 | 0.39 | 0.02 | 0.03 | 0.05 | 0.16 | 0.04 | 2.6 | 1.7 | 3.0 | 1.1 | 5.2 | <0.02 | <0.01 | <0.01 |
| | 2 | 29.0 | 34.4 | 0.36 | 0.03 | <0.01 | 0.12 | 0.11 | 0.05 | 1.6 | 1.7 | 2.4 | 1.2 | | | | |
| F | 1 | 54.0 | 17.3 | 0.33 | 0.06 | 0.04 | 0.21 | 0.04 | 0.04 | 0.40 | 1.1 | 1.8 | 2.4 | 5.4 | 0.02 | 0.01 | 0.01 |
| | 2 | 49.4 | 20.3 | 0.42 | 0.08 | 0.04 | 0.17 | 0.04 | 0.09 | 1.2 | 1.5 | 6.0 | 3.1 | | | | |
| H | 1 | 30.7 | 49.3 | 0.16 | 0.03 | 0.02 | 0.01 | 0.06 | 0.11 | 1.0 | 4.8 | 3.2 | 1.4 | 5.4 | <0.02 | <0.01 | <0.01 |
| | 2 | 26.7 | 46.7 | 0.21 | 0.02 | 0.01 | 0.02 | 0.08 | 0.13 | 1.6 | 6.1 | 5.4 | 1.8 | | | | |
| | 3 | 35.6 | 44.8 | 0.31 | 0.03 | 0.02 | 0.03 | 0.06 | 0.11 | 1.3 | 5.6 | 3.4 | 1.5 | | | | |
| | 4 | 25.8 | 50.7 | 0.34 | 0.02 | <0.01 | 0.02 | 0.04 | 0.08 | 1.0 | 0.8 | 2.7 | 0.65 | | | | |
| I | 1 | 20.8 | 32.2 | 0.29 | 0.01 | 0.04 | 0.01 | 1.52 | 0.11 | 0.63 | 2.4 | 8.7 | 2.5 | 11.1 | <0.02 | <0.01 | <0.01 |
| | 2 | 20.0 | 37.4 | 0.75 | 0.01 | 0.04 | 0.01 | 0.42 | 0.01 | 0.02 | 2.4 | 7.1 | 1.9 | | | | |
| | 3 | 16.8 | 43.7 | 0.10 | 0.01 | 0.04 | 0.01 | 0.77 | 0.08 | 0.66 | 2.5 | 7.2 | 2.2 | | | | |
| | 4 | 20.7 | 28.7 | 0.35 | 0.01 | 0.04 | 0.02 | 1.02 | 0.07 | 0.80 | 1.7 | 8.2 | 2.2 | | | | |
| L | 1 | 46.8 | 20.0 | 0.23 | 0.15 | 0.02 | 0.02 | 0.20 | 0.15 | 1.8 | 6.7 | 3.7 | 2.2 | 7.2 | <0.02 | <0.01 | <0.01 |
| | 2 | 29.8 | 46.7 | 0.57 | 0.09 | <0.01 | 0.02 | 0.18 | 0.33 | 2.7 | 7.6 | 8.9 | 2.1 | | | | |
| | 3 | 37.6 | 37.6 | 0.63 | 0.05 | 0.03 | 0.02 | 0.15 | 0.51 | 2.5 | 2.4 | 9.3 | 2.1 | | | | |
| | 4 | 20.4 | 53.6 | 0.66 | 0.09 | 0.04 | 0.02 | 0.17 | 0.22 | 3.0 | 7.6 | 11.0 | 2.6 | | | | |

Table 3.3-1 CHEMICAL ANALYSES OF BLAST FURNACE RESIDUES - SLUDGES PART 2
(weight %)

| Plant | Sample | Fe | C | S | Pb | Sn | Zn | Mn | $Na_2O$ | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ | As | Sb | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | 29.4 | 29.3 | 0.47 | 0.09 | 0.01 | 1.11 | 0.06 | 0.07 | 1.6 | 3.6 | 5.3 | 2.5 | 9.3 | <0.02 | <0.01 | <0.01 |
| | 2 | 26.5 | 27.7 | 0.45 | 0.09 | 0.02 | 0.50 | 0.09 | 0.08 | 1.9 | 4.7 | 4.4 | 2.4 | | | | |
| | 3 | 25.6 | 26.0 | 0.44 | 0.13 | <0.01 | 0.86 | 0.14 | 0.07 | 1.3 | 4.0 | 5.0 | 3.0 | | | | |
| | 4 | 27.2 | 29.8 | 0.19 | 0.11 | <0.01 | 1.04 | 0.13 | 0.05 | 1.1 | 3.0 | 5.0 | 2.7 | | | | |
| D | 1 | 21.8 | 40.9 | 0.25 | 0.10 | 0.06 | 1.6 | 0.07 | 0.11 | 1.9 | 2.6 | 3.2 | 1.8 | 9.7 | <0.02 | ≤0.01 | <0.01 |
| E | 1 | 40.7 | 24.3 | 0.46 | 0.19 | 0.02 | 0.26 | 0.17 | 0.04 | 1.2 | 3.1 | 3.2 | 1.2 | 6.2 | <0.02 | <0.01 | <0.01 |
| | 2 | 43.0 | 21.1 | 0.46 | 0.13 | 0.03 | 0.38 | 0.10 | 0.04 | 0.87 | 2.1 | 2.8 | 0.86 | | | | |
| F | 1 | 39.6 | 18.3 | 0.78 | .092 | 0.05 | 2.1 | 0.01 | 0.08 | 0.65 | 0.30 | 4.0 | 2.3 | 6.5 | <0.02 | <0.01 | 0.01 |
| | 2 | 38.9 | 18.9 | 0.94 | 1.02 | 0.04 | 2.6 | 0.02 | 0.09 | 0.92 | 0.28 | 3.5 | 2.2 | | | | |
| I | 1 | 30.3 | 30.2 | 0.25 | 0.05 | 0.03 | 0.04 | 0.26 | 0.03 | 0.41 | 1.7 | 5.6 | 2.0 | 7.8 | <0.02 | <0.01 | 0.01 |
| | 2 | 30.2 | 31.4 | 0.31 | 0.04 | 0.02 | 0.06 | 0.17 | 0.04 | 0.60 | 2.0 | 5.1 | 1.8 | | | | |
| | 3 | 30.4 | 34.3 | 0.26 | 0.05 | 0.03 | 0.06 | 0.29 | 0.04 | 0.49 | 2.2 | 4.0 | 1.5 | | | | |
| | 4 | 24.7 | 40.5 | 0.68 | 0.04 | 0.02 | 0.07 | 0.10 | 0.03 | 0.46 | 2.1 | 4.7 | 1.5 | | | | |
| M | 1 | 32.5 | 32.5 | 0.63 | 0.05 | 0.01 | 0.08 | 0.15 | 0.08 | 0.48 | 1.8 | 4.7 | 1.2 | 7.5 | <0.02 | <0.01 | 0.01 |
| | 2 | 28.5 | 32.3 | 0.86 | 0.05 | 0.01 | 0.14 | 0.09 | 0.03 | 1.2 | 2.3 | 6.3 | 1.7 | | | | |
| | 3 | 27.5 | 35.1 | 0.93 | 0.06 | 0.03 | 0.12 | 0.06 | 0.07 | 0.69 | 2.0 | 6.8 | 1.8 | | | | |
| | 4 | 35.6 | 20.9 | 1.01 | 0.07 | 0.03 | 0.11 | 0.17 | 0.04 | 0.61 | 2.2 | 8.2 | 1.9 | | | | |

Table 3.3-2 CHEMICAL ANALYSES OF BLAST FURNACE RESIDUES (FROM THE LITERATURE)
(% dry basis)

| Ref. | Fe | C | S | Pb | Sn | Zn | Mn | NagO | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ | As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3[a, d] | 20.0/<br>49.9 | 6.6/<br>50.0 | - | 0.001/<br>0.28 | - | 0.08/<br>2.7 | - | 0.095/<br>0.52 | 0.48/<br>1.82 | - | - | - | - | - |
| 3[a, e] | 5.9/<br>43 | 11.2/<br>33.9 | - | 0.05/<br>3.4 | - | <0.08/<br>11.5 | - | <0.04/<br>1.4 | 0.30/<br>5.4 | - | - | - | - | - |
| 5[b] | 45 | 5.5 | 4.6 | 0.03 | 0.01 | 0.2 | - | - | - | 6.2 | 7.7 | - | - | 0.007 |
| 6[b] | 28.6 | 40.8 | 0.3 | - | - | 0.54 | 0.3 | - | - | 3.0 | 2.7 | 0.7 | 6.1 | - |
| 6[a] | 32.2 | 38.5 | 0.2 | - | - | 0.45 | 0.5 | - | - | 2.5 | 3.1 | 0.7 | 6.9 | - |
| 7[a] | 27.0 | 21.4 | - | 0.01 | - | 0.05 | 1.1 | - | - | 1.2 | 5.2 | 2.2 | 7.3 | - |
| 8[b, c] | 27.5 | 17.8 | 2.0 | 4.2 | - | 9.5 | - | - | - | - | - | - | - | - |
| 9[a] | 23.6 | 41.1 | 0.22 | 0.01 | - | 0.08 | - | - | - | - | - | - | - | - |
| 10[b] | 40.2/<br>61.0 | 1.1/<br>16.0 | 0.08/<br>0.3 | - | - | 0.2/<br>0.3 | - | - | - | 2.1/<br>3.9 | 3.1/<br>4.6 | 0.9/<br>5.9 | 4.1/<br>8.5 | - |
| 11[b] | 20.0/<br>25.0 | 17.0/<br>18.0 | - | 0.2/<br>0.3 | - | 9.0/<br>10.5 | - | - | - | - | - | - | - | - |
| 12[h] | 33.6 | 23.3 | - | 0.3 | - | 0.7 | 0.4 | - | 0.5 | 2.8 | 7.5 | 1.1 | 10.5 | - |
| 12[a] | 31.5 | 30.0 | 0.7 | 0.3 | - | 0.7 | 0.4 | - | 0.5 | 2.6 | 7.0 | 1.0 | 9.8 | - |
| 12[a] | 40.0 | 10.0 | 0.2 | 0.2 | - | 0.8 | 0.3 | - | 1.5 | 6.5 | 6.0 | 1.2 | 11.0 | - |
| 12[a] | 51.0 | 10.3 | 0.3 | 0.2 | - | 0.8 | 0.8 | - | 1.5 | 4.0 | 6.0 | 2.0 | 10.5 | - |
| 13[a] | 50.0 | 11.0 | 0.2 | 0.1 | - | 0.8 | - | - | 0.2 | - | 4.5 | 0.9 | 6.8 | - |
| 14[a] | 29.0 | 25.4 | 0.54 | <0.05 | - | 0.15 | 0.34 | 6.4 | - | 13.2 | 9.4 | 0.07 | 11.6 | - |
| 15[a, c] | 43 | 2.5 | 3.4 | 0.02 | 0.01 | 0.4 | - | - | - | 3.8 | - | - | - | 0.001 |

a Dust
b Slurry or sludge
c Average
d Primary
e Secondary

Table 3.3-3 PARTICLE SIZE DISTRIBUTION OF BLAST FURNACE DUST & SLUDGES

(Cumulative Percent Retained on Screen)

| Screen | Dusts at Plant | | | | | | Sludges at Plant | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | E | F | H | I | L | C | D | E | F | I | M |
| 8 mesh | T | - | - | 0.2% | - | 2.0% | - | - | - | - | - | - |
| 16 mesh | 0.2% | 0.7% | T | 2.2 | 0.1% | 3.3 | - | - | - | - | - | - |
| 30 mesh | 2.2 | 2.4 | 0.6 | 10.7 | 3.1 | 8.2 | 0.1% | - | - | - | - | - |
| 50 mesh | 22.7 | 12.5 | 5.9 | 39.5 | 25.3 | 34.9 | 0.2 | T | - | - | 1.0% | - |
| 100 mesh | 67.1 | 46.5 | 25.4 | 70.4 | 70.5 | 69.0 | 5.4 | 4.5% | - | - | 8.9 | - |
| 200 mesh | 89.5 | 77.3 | 66.0 | 86.3 | 89.2 | 91.0 | 38.0 | 32.8 | - | - | 24.4 | - |
| 323 mesh | 94.6 | 89.8 | 94.0 | 93.8 | 93.8 | 95.9 | 56.0 | 56.2 | - | - | 38.7 | |
| 325 mesh[a] | 97.6 | 86.6 | 93.5 | 87.3 | 92.4 | 95.5 | 33.9 | 50.9 | 27.3% | 30.0% | 33.5 | 38.2% |
| 20 micron | 98.5 | 97.2 | 98.8 | 98.5 | 97.4 | 98.8 | 57.9 | 72.4 | 52.2 | 73.5 | 78.5 | 62.4 |
| 10 micron | 99.2 | 98.1 | 99.4 | 100.0 | 98.3 | 99.8 | 66.3 | 81.7 | 70.0 | 84.3 | 88.5 | 75.0 |

[a] Separate screening of another portion of sample.

The tramp element content also varied, coincidentally: zinc between 0.1-2.6%, Pb from trace to 1.02%, and the alkali ($K_2O + Na_2O$) content between 0.43 and 10.6%.

The chemical analyses of blast furnace dusts, sludges and slurries reported in the literature show similar variation in composition (Table 3.3-2).

As part of our study, we also ran size analyses on selected samples to aid in determining how these materials might fit into possible recycling processes that could be suggested for better utilization of the potential represented by these waste residues. The particle size distribution of the collected samples is presented in Table 3.3-3.

We found a wide variation from plant to plant in the quantities of dusts and sludges (dry basis) collected (Table 3.3-4).

Table 3.3-4 BLAST FURNACE DUST AND SLUDGE (RESIDUES) COLLECTED (1974)

% OF IRON PRODUCTION

| Plant | Dust % | Sludge % | Total % |
|---|---|---|---|
| A | 2.8 | 0.8 | 3.6 |
| C | 2.3 | 0.2 | 2.5 |
| D | 3.4 | 1.1 | 4.5 |
| E | 3.4 | 0.5 | 3.9 |
| F | 1.8 | 1.0 | 2.8 |
| G | 0.8 | 1.3 | 2.1 |
| H | 1.5 | 1.2 | 2.8 |
| I | 0.8 | 1.6 | 2.4 |
| J | 1.0 | 2.8 | 3.8 |
| K | 0.7 | 0.8 | 1.6 |
| Weighted Avg. | 1.55 | 1.37 | 2.9 |

Six of the ten plants we visited with BF shops recycle all of their dusts and sludges to sinter. The balance of the plants recycle or store their dusts and landfill or stock their sludges (Table 3.3-5).

Table 3.3-5 BLAST FURNACE RESIDUES DISPOSITION - 1974

| Plant | Disposition: Dust | Disposition: Sludge |
|---|---|---|
| A | Recycle - sinter | Recycle - sinter |
| C | Recycle - sinter | Recycle - sinter |
| D | Recycle - sinter | Landfill |
| E | Recycle - sinter | Recycle - sinter |
| F | 50% sale or sinter,<br>50% stock | Landfill |
| G | Storage | Landfill |
| H | Recycle - sinter | Storage |
| I | Recycle - sinter | Recycle - sinter |
| J | Recycle - sinter | Recycle - sinter |
| K | Recycle - sinter | Recycle - sinter |

On a combined basis, the present disposition of the waste residues is as follows:

| Weighted Averages | |
|---|---|
| Recycle - sinter | 77.4% |
| Landfill | 13.3% |
| Stock | 9.3% |

The problems in recycling BF dusts and sludges are covered in Section 3.16, Recycling.

The blast furnace off-gas cleaning practices are essentially the same in England, Germany and Japan as in the U.S. In the works we visited in these countries, "primary dusts" are usually collected in dust catchers and sometimes in dry cyclones. Subsequently, the BF gases are further cleaned in wet scrubbers and/or wet-type electrostatic precipitators. In some operations in Germany, wet electrostatic precipitators are used in combination with baghouses for the same purpose.

The only major difference in the pollution control of the BF operations between the U.S. and foreign plants visited is that the largest and most modern blast furnaces in Japan also have tap hole, runner and casthouse dedusting and degassing pollution control units. The pollution control equipment used for these dedusting and degassing operations on older units include "wet rotocyclones," "dry air tumblers," and baghouses.

The quantities of residues generated in the BF operations of the different countries are presented in Table 3.3-6.

The residual loads associated with blast furnace operations based on the OECD, ED 1975 study are given in Table 3.3-7.

Table 3.3-6 TYPICAL RANGES OF QUANTITIES OF RESIDUES COLLECTED IN BF OPERATIONS BY COUNTRIES
(kg/ton dry basis)

| | | |
|---|---|---|
| United tes | 16-45 | (33[a]) |
| England | 25-50 | |
| Germany | 20-55 | |
| Japan | 7-35 | |

[a] U.S. average in 1974(1)

Table 3.3-7 RAW RESIDUAL LOADS ASSOCIATED WITH BLAST FURNACE OPERATIONS(17)

| Type of Discharge | Raw Residual Load (kg/ton of iron) |
|---|---|
| Airborne residuals | |
| Particulates | 0.2 - 1.6 |
| Waterborne residuals | |
| (effluent flow, lit./ton) | (16,263) |
| Ammonia | 0.2 |
| Phenol | 0.02 |
| Cyanide | 0.03 |
| Sulphide | 0.3 |
| Suspended solids | 26.0 |
| Fluoride | 0.08 |
| (pH) | (7 - 9) |

The relatively lower residue quantities generated in the Japanese ironmaking facilities are attributed by the Japanese experts(5,11) to two main differences in their BF operations: (1) the data supplied to us were from some of the world's largest and most modern ironmaking furnaces, and (2) the Japanese in the visited blast furnace operations use higher sinter ratios than elsewhere in the world. The same experts noted that when they have to switch from the high (i.e., 80-90%) sinter ratio (yielding a low 7-10 kg/ton residue) to a lower (e.g., 70%) sinter ratio, the generated dust quantity increases to 15-16 kg/ton of iron produced even in their large (11,000 tons/day) blast furnaces.

While our study showed that an average of 77.4% of the total BF pollution control residues generated in the U.S. are recycled, the British Steel Corporation recycled about 50% of their residues (73% of their dry and 22% of their wet residues). The Germans recycled almost 94%(4) and the Japanese(5) more than 90%, mainly through sintering operations or "reduced pellet" operations.

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## 3.4 SUBCATEGORY: BLAST FURNACE (FERROMANGANESE)

This subcategory was established for this study because a previous EPA study(1) covered in a separate subcategory the ferromanganese operations, and we also visited one plant that had a companion operation where one blast furnace had been recently used for ferromanganese production. Most ferroalloys are now made in electric furnaces. Coincidentally, there were only two BF ferromanganese operations in the U.S. in 1974(2).

The gas cleaning circuit used on this furnace consists of a dust catcher, venturi scrubber and gas cleaning tower. The water circuit is closed with the overflow from a 110' diameter thickener being recycled to the scrubber and tower. Thickener underflow passes to a vacuum filter. Fifty-seven kg (104 lbs.) of dust and 114 kg (228 lbs.) of dry sludge/ton of ferromanganese produced are collected. The fresh filter cake contains roughly 35% moisture and is deposited in a tar-lined (based) pit at their dump site. Collected dust is sold for conversion to briquettes or pellets such as BOF feed.

Samples of the dust and sludge were provided and chemical and sieve analyses were made. These data are presented in Tables 3.4-1 and 3.4-2. It should be kept in mind that these samples were collected from storage or disposal piles that had been sitting for well over a year since this furnace had not been in ferromanganese production since 1974.

In none of the plants visited in England, Germany and Japan did they have blast furnace ferromanganese production nor did the Verein Deutscher Eisenhuttenleute and the Japan Iron and Steel Federation have information available on the residues produced in these operations. In general, we were informed that the quantities generated in BF ferromanganese production are very small and negligible when compared with the quantities arising in other types of pollution control operations of the steel mills. Even when residues generated in electric arc

Table 3.4-1 CHEMICAL ANALYSES OF BF FERROMANGANESE DUST & SLUDGE
(% dry basis)

| | Zn | Pb | Sn | Al | K | Mg | Ca | Mn | Na | C | Moisture | Total Fe | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sludge | .41 | .04 | .06 | 3.61 | 7.49 | 1.93 | 6.95 | 6.86 | .51 | 7.4 | 26.4 | 2.4 | 5.42 |
| | .37 | .04 | .04 | 3.55 | 8.74 | 1.70 | 6.38 | 5.75 | .48 | 7.6 | 27.4 | 1.4 | 5.41 |
| Dust | .16 | .01 | .04 | 5.05 | 1.87 | .28 | 1.91 | 19.36 | .07 | 9.5 | - | 4.8 | 6.17 |
| | .17 | .01 | .04 | 5.05 | 2.87 | .25 | 1.68 | 21.22 | .05 | 7.1 | - | 5.3 | 6.8 |

Table 3.4-2 PARTICLE SIZE ANALYSES OF BF FERROMANGANESE DUST AND SLUDGE
(Cumulative Percent Retained on Screen)

Sludge

| Screen Sizing | | Sample 1 | Sample 2 |
|---|---|---|---|
| Sludge | 44 micron | 3.5% | 4.6% |
| | 20 micron | 11.1 | 11.3 |
| | 10 micron | 24.3 | 24.6 |

Dust

| Screen Sizing | | Sample 1 | Sample 2 |
|---|---|---|---|
| Dust | 8 mesh | 0.1% | - |
| | 16 mesh | .2 | .1% |
| | 30 mesh | 4.7 | 3.2 |
| | 50 mesh | 28.0 | 22.8 |
| | 100 mesh | 62.1 | 63.5 |
| | 200 mesh | 84.1 | 89.4 |
| | 325 mesh | 92.4 | 94.9 |

furnace ferromanganese production are considered, the total quantity of this type of residue was regarded as "small." Since the residue quantities are small and are usually recycled or sold, the representatives of the foreign steel industry and iron and steel works whom we visited were not aware of any problem in the disposal of these residues.

However, after our visit to the BSC in England, the following information was obtained(3): The BSC ferromanganese blast furnace production, centered on Teesside in the northeast of England, was 191,000 tons/year in 1974-75.

> "...6,200 tons of primary dust were collected dry, but the pyrophoric nature of this material means it is very difficult to handle and, therefore, is wetted to form a slurry. This slurry is combined from solids arising from secondary cleaning to yield approximately 19,000 tons of solids containing 40% moisture and approximately 25% of manganese dry weight. These solids contain unacceptable amounts of cyanide and alkali. Current practice is to dump."

## 3.4 REFERENCES - BLAST FURNACE (FERROMANGANESE)

1) Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category. EPA 440/1-73/024. U.S. EPA, 1974.

2) Annual Statistical Report for 1974. American Iron and Steel Institute, Washington, D.C., 1975.

3) Private communication from John M. Campbell of the British Steel Corporation.

## 3.5 SUBCATEGORY: BASIC OXYGEN FURNACE (BOF)

The continuing phase-out of the open hearth furnaces (OH) is the result of the development in the early 1950's of the basic oxygen process (BOF)(1). The latter is faster, requires no supplementary fuel addition, and is specifically designed for the efficient utilization of oxygen. Its one drawback is an inability to process as much scrap as the OH furnaces since process heat availability limits it to 30% or less scrap in the charge.

The basic oxygen furnace is a cylindrical or barrel-shaped refractory-lined vessel with a closed bottom and a reduced diameter but nonetheless open top through which the charge and oxygen are added. The vessel is mounted on trunions and is tiltable so that molten steel can be poured (tapped) out of an upper side tap hole when rotated in one direction and slag can be discharged with full inversion of the vessel with counter rotation.*

Scrap and hot metal constitute the charge which is added to the slightly tilted vessel. The scrap is charged first, followed by the molten iron. The vessel is then raised to a vertical position, the lance inserted and the oxygen blow is begun. Following this, the flux additions (lime and fluorspar) are made through an overhead chute projecting through a water-cooled hood surrounding the lance and open end of the vessel. The hood, in turn, is connected to an exhaust fan. Tap-to-tap time is in the order of one hour or less.

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* United States Steel Corporation has developed a modified version of this process using a bottom blown vessel which they call the Q-BOP process. This became practical with a breakthrough in bottom design allowing the blowing of oxygen without excessive bottom erosion. This approach is said to yield slightly more steel (less loss) and lower nitrogen, carbon and sulfur levels in the finished steel than the normal BOP. One of the eight plants we visited using basic oxygen furnaces had Q-BOP operations.

Basic oxygen furnaces are built in a wide variety of sizes ranging from roughly 50 tons to 350 tons per heat. As is the case with blast furnaces, the newer BOF's are usually of the larger capacities. In 1974 81,522,000 tons of carbon and alloy steels were produced in these furnaces(21). This represents about 56% of the total U.S. steel production for the year.

Our study took us to eight plants having a total of 20 BOP vessels. They ranged in size from 130 to 335 tons/heat. Two of these units were Q-BOP types rated at 200 tons/heat.

Oxygen blowing inherent to the process generates substantial quantities of very fine particles that are carried out of the vessel in the off-gas. Wet, semi-wet and dry systems are used for removing the particulate matter from the gas stream.

A recent EPA Development Document(2) covered the BOF operations in two subcategories (wet and semi-wet). But for our purposes, a single subcategory was more preferred because the residues generated in wet or semi-wet BOF pollution control facilities are similar in compositions and quantities.

The wet systems normally utilize venturi scrubber(s) in conjunction with prior gas conditioning in a "wet spark box" or "quencher." A dry electrostatic precipitator is substituted for the scrubber in the semi-wet approach (after "wet" gas conditioning). Dry electrostatic precipitators are also used for the final cleaning of the off-gases in the dry system, rather than baghouses. Six of the eight installations we visited used the wet system, one a semi-wet and the remaining plant, a dry system. The Q-BOP shop (wet) had a dust leg to remove the coarser particles ahead of their quencher and scrubber.

The wet gas cleaning circuit yields two residues: a coarse product ("sands") and a fine product ("fines"). Settling basins or tanks, usually fitted with rakes, are used to remove the former, and classifiers and thickeners followed by filtering for the latter. Flocculation polymers are generally added to facilitate the settling of the fines. The semi-wet circuit, of course, yields a wet coarse fraction and dry fines (dust). In the dry systems, both the coarse and fine fractions are dry. In all cases, both the coarse and fine residues were, in effect if not in practice, considered as one type from a disposal or reuse standpoint.

Many shops have an additional dry collection system to handle emissions during charging and tapping; four of the eight we visited did. These are invariably baghouse operations that collect a rather small amount of dust over a period of a year. Brinn(3) reports that these emissions are in the order of 0.07 kg/ton of metal poured. Our findings (approximate) were: .13, .19, .01 and .15 kg/ton for the respective plants.

The results of the chemical analyses of the dust and sludge samples collected or obtained for this study are given in Table 3.5-1 (fines) and 3.5-2 (sands). As can be seen from these results, the chemical compositions of the BOF residues vary considerably. The iron content in most cases is between 50 and 60%; however, values as low as 32.4% and as high as 66.4% were encountered in our samples. The variation in zinc is even greater, from 0.01% to as high as 13-14%.

The variation in chemical composition of residues is attributed to the variation in the raw materials used in BOF steelmaking, e.g., the more zinc or lead containing scrap used, the higher the zinc and lead content of the residues will be. This is due to the fact that during steelmaking the zinc and lead, having low boiling points, easily volatilize, and after oxidation in the air, or oxygen mixture, are recovered as dusts during the BOF off-gas cleaning operations.

Table 3.5-1 CHEMICAL ANALYSES OF BOF RESIDUES - FINES
(weight % - dry)

| Plant | Sample | Fe | C | S | Pb | Sn | Zn | Mn | $Na_2O$ | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ | As | Sb | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| E[a] | Slurry[b] | | | | | | | | | | | | | | | | |
| | 1 | 45.2 | 2.9 | 0.16 | [illegible] | 0.02 | 12.8 | 0.56 | 0.07 | 0.27 | 0.30 | 5.6 | 0.66 | 1.8 | <0.02 | <0.01 | <0.01 |
| | 2 | 43.9 | 3.1 | 0.44 | 0.09 | 0.04 | 13.7 | 0.55 | 0.05 | 0.23 | 0.25 | 5.9 | 0.60 | | | | |
| F | Dust[c] | | | | | | | | | | | | | | | | |
| | 1 | 58.3 | 2.7 | 0.04 | 0.05 | 0.02 | 0.24 | 0.12 | 0.27 | 1.2 | 0.09 | 7.6 | 0.61 | 2.8 | <0.02 | <0.01 | <0.01 |
| | 2 | 66.6 | 0.5 | 0.01 | 0.04 | 0.03 | 0.12 | 0.13 | 0.35 | 0.70 | 0.05 | 6.0 | 0.61 | | | | |
| G | Sludge[b] | | | | | | | | | | | | | | | | |
| | 1 | 60.2 | 1.4 | 0.20 | 1.8 | 0.06 | 2.0 | 0.50 | 0.11 | 0.31 | 0.08 | 3.6 | 0.58 | 1.6 | <0.02 | <0.01 | <0.01 |
| | 2 | 60.7 | 1.5 | 0.17 | 1.7 | 0.04 | 1.7 | 0.52 | 0.07 | 0.29 | 0.09 | 4.2 | 0.99 | | | | |
| | 3 | 61.9 | 1.3 | 0.15 | 1.6 | 0.04 | 1.6 | 0.41 | 0.07 | 0.22 | 0.11 | 3.4 | 0.80 | | | | |
| | 4 | 61.6 | 1.2 | 0.13 | 1.4 | <0.01 | 1.4 | 0.37 | 0.07 | 0.27 | 0.08 | 3.6 | 0.75 | | | | |
| I | Sludge[b] | | | | | | | | | | | | | | | | |
| | 1 | [illegible] | 1.7 | 0.14 | 0.04 | <0.01 | 0.07 | 0.36 | 0.11 | 0.12 | 0.11 | 6.9 | 2.0 | 2.3 | <0.02 | <0.01 | <0.01 |
| | 2 | 56.5 | 1.4 | 0.13 | 0.07 | <0.01 | 0.07 | 0.50 | 0.09 | 0.12 | 0.08 | 6.1 | 2.4 | | | | |
| | 3 | 57.6 | 1.3 | 0.13 | 0.06 | <0.01 | 0.09 | 0.59 | 0.11 | 0.12 | 0.06 | 5.7 | 2.0 | | | | |
| | 4 | 55.6 | 1.6 | 0.11 | 0.05 | <0.01 | 0.07 | 0.34 | 0.09 | 0.12 | 0.09 | 6.5 | 2.6 | | | | |
| [illegible] | Sludge[b] | | | | | | | | | | | | | | | | |
| | 1 | [illegible] | 1.5 | [illegible] | 0.71 | 0.05 | 4.5 | 0.12 | 0.16 | 0.35 | 0.17 | 6.0 | 1.1 | 2.0 | <0.02 | <0.01 | <0.01 |
| | 2 | [illegible] | 1.5 | [illegible] | 0.40 | 0.04 | 3.5 | 0.08 | 0.13 | 0.47 | 0.55 | 6.9 | 1.2 | | | | |
| | 3 | 57.3 | 1.1 | 0.07 | 0.29 | 0.01 | 1.4 | 0.14 | 0.11 | 0.27 | 0.17 | 6.4 | 1.4 | | | | |
| | 4 | 56.2 | 2.6 | 0.15 | 0.60 | 0.02 | 3.7 | 0.35 | 0.13 | 0.37 | 0.25 | 4.6 | 1.0 | | | | |

a Q-BOP b Scrubber c ESP

## Table 3.5-2 CHEMICAL ANALYSES OF BOF RESIDUES - SANDS
(weight % - dry)

| Plant | Sample | Fe | C | S | Pb | Sn | Zn | Mn | $Na_2O$ | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ | As | Sb | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A[b] | Filter cake[a] | | | | | | | | | | | | | | | | |
| | 1 | 59.1 | 0.9 | 0.02 | 0.02 | 0.10 | 0.01 | 0.61 | 0.03 | 0.03 | 0.13 | 15.9 | 2.0 | 3.4 | <0.02 | <0.01 | <0.01 |
| | 2 | 50.6 | 1.5 | 0.04 | 0.21 | 0.10 | 0.01 | 0.52 | 0.11 | 0.16 | 0.38 | 11.4 | 1.8 | | | | |
| B[c] | Sludge[b] | | | | | | | | | | | | | | | | |
| | 1 | 35.0 | 1.0 | 0.06 | 0.01 | 0.02 | 0.3 | 0.67 | 0.05 | 0.14 | 0.62 | 23.7 | 2.1 | 13.0 | <0.02 | <0.01 | <0.01 |
| | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | 0.72 | 0.03 | 0.16 | 0.53 | 20.8 | 1.6 | | | | |
| I | Sludge[d] | | | | | | | | | | | | | | | | |
| | 1 | 52.9 | 1.6 | 0.10 | <0.01 | 0.02 | 0.01 | 0.32 | 0.04 | 0.08 | 0.25 | 16.1 | 8.3 | 2.8 | <0.02 | <0.01 | <0.01 |
| | 2 | 46.1 | 1.1 | 0.09 | 0.01 | 0.02 | 0.01 | 0.28 | 0.03 | 0.07 | 0.21 | 15.2 | 4.8 | | | | |
| | 3 | 47.3 | 1.0 | 0.06 | <0.01 | 0.01 | 0.01 | 0.36 | 0.03 | 0.05 | 0.25 | 15.4 | 5.7 | | | | |
| | 4 | 55.5 | 0.9 | 0.02 | <0.01 | 0.01 | 0.01 | 0.88 | 0.01 | 0.05 | 0.25 | 13.8 | 3.6 | | | | |
| J | Sludge[d] | | | | | | | | | | | | | | | | |
| | 1 | 53.7 | 0.6 | <0.01 | <0.01 | <0.01 | 0.03 | 0.16 | 0.01 | 0.01 | 0.15 | 5.4 | 1.7 | 3.7 | <0.02 | <0.02 | <0.01 |
| | 2 | 66.4 | 0.4 | <0.01 | <0.01 | 0.01 | 0.05 | 0.25 | <0.01 | 0.01 | 0.08 | 2.8 | 0.79 | | | | |
| | 3 | 61.6 | 0.7 | 0.01 | 0.01 | <0.01 | 0.05 | 0.47 | 0.01 | 0.01 | 0.13 | 5.4 | 1.8 | | | | |
| | 4 | 59.3 | 0.5 | 0.01 | 0.01 | 0.01 | 0.08 | 0.33 | 0.01 | 0.01 | 0.15 | 9.2 | 2.1 | | | | |

a Rake classifier and scrubber fines combined.

b Settling basin

c C-BOP

d Rake classifer.

Table 3.5-3 CHEMICAL ANALYSES OF BOF RESIDUES (FROM LITERATURE)
(% dry basis)

| Ref. | Fe | C | S | Pb | Sn | Zn | Mn | NagO | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3[d] | 52.2 | 1.0 | - | - | - | - | 0.93 | - | 0.1 | 0.8 | 11.1 | 1.8 | 2.2 |
| (R) 4 | 52.0/<br>56.1 | Trace/<br>1.3 | 0.1/<br>2.0 | Trace/<br>0.29 | Trace/<br>0.46 | Trace/<br>3.6 | 0.31/<br>1.3 | | | Trace/<br>3.6 | 0.3/<br>7.9 | 0.15/<br>2.6 | 0.34/<br>1.8 |
| 5[b] | 60 | - | 0.7 | 0.3 | - | 3.0 | - | - | - | 0.04 | 5.0 | - | - |
| 6[a] | 56.5 | 1.45 | 0.06 | 0.09 | - | 2.0 | 1.0 | - | - | 0.25 | 4.0 | 1.6 | 1.7 |
| (R) 7[c] | 50.5/<br>79.2 | Trace/<br>0.55 | 0.03/<br>1.4 | 0.21/<br>0.79 | - | 2.37/<br>15.1 | 0.25/<br>0.95 | - | - | Trace/<br>0.2 | 0.75/<br>5.2 | 0.11/<br>0.37 | 0.65/<br>1.2 |
| 8[c] | 64.8 | - | 0.03 | - | - | 1.1 | - | - | - | 0.1 | 1.8 | 0.1 | 1.7 |
| 9[c] | 57.1 | 0.56 | - | 0.001 | - | 5.1 | 0.93 | - | - | 0.10 | 2.9 | 0.56 | 1.7 |
| (A) 10[c] | 55.7 | 0 | 0.2 | 0.3 | - | 1.5 | - | - | - | - | 6.0 | 0.3 | 1.7 |
| 10[c] | 55.7 | 0.44 | 0.11 | 0.44 | - | 6.3 | - | - | - | - | - | - | - |
| (A) 10[c] | 54.0 | - | - | 0.4 | - | 3.0 | 1.0 | - | - | - | - | - | - |
| 11[d] | 59.0 | 0.2 | 0.6 | - | - | - | 2.0 | - | - | - | 2.0 | - | 1.0 |
| 11[d] | 75.0 | 0.2 | 0.5 | - | - | - | 2.0 | - | - | - | 2.0 | - | 1.0 |
| (R) 12[d] | 41.3/<br>53.0 | 0.8/<br>6.1 | 0.1/<br>0.2 | - | - | 0.3/<br>7.1 | - | - | - | 0.6/<br>1.8 | 12.2/<br>15.9 | 1.8/<br>8.6 | 1.9/<br>2.5 |
| 13[d] | 62.0 | 0.1 | 0.3 | 0.3 | - | 2.8 | - | - | 0.3 | - | 1.4 | 0.7 | 0.9 |
| 13[c] | 54.5 | 0.2 | 0.2 | 0.2 | - | 0.4/<br>2.0 | - | - | 0.6 | - | 12.5 | 0.5 | 1.4 |
| 14[d] | 64.1 | - | 0.5 | - | - | 0.4 | - | - | - | - | 1.5 | - | 1.1 |
| 15[d] | 56.0 | - | 0.1 | - | - | 0.5 | - | - | - | 0.4 | 12.5 | 1.3 | 2.4 |
| 16[c] | 55.7 | 0.44 | 0.11 | 0.4 | - | 6.3 | 0.54 | 0.34 | - | 3.0 | 5.3 | 0.50 | 4.7 |
| (R) 17[c] | 47.0/<br>63.6 | 0.2/<br>1.0 | - | 0.19/<br>0.75 | - | 0.16/<br>2.5 | - | 0.47 | 0.15 | - | - | - | - |

a Raw fume  b Slurry  c Dust  d Fines  (A) Average  (R) Range of composition reported in reference

Table 3.5-4 PARTICLE SIZE ANALYSES OF BOF RESIDUES

(Cumulative Percent Retained on Screen)

| Screen | Fines (Sludge or Dust) at Plant | | | | | | | Sands at Plant | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | E | F | G | I | K | L | M | A | E | I | J |
| 6 mesh | | | | | | | | - | - | - | - |
| 16 mesh | | | | | | | | - | 0.1% | - | 1.1% |
| 30 mesh | | | | | | | | 1.9% | 6.5 | 0.1% | 5.4 |
| 50 mesh | | | | | | | | 9.4 | 32.2 | 10.3 | 21.0 |
| 100 mesh | | | | | | | | 33.0 | 62.3 | 33.9 | 67.1 |
| 200 mesh | | | | | | | | 70.9 | 83.9 | 66.8 | 93.5 |
| 325 mesh | | | | | | | | 86.9 | 92.4 | 82.0 | 96.4 |
| 325 mesh[a] | 4.6% | 26.7% | 20.5% | 11.4% | 19.9% | 7.9% | 3.2% | 83.3 | 92.2 | 74.1 | 96.6 |
| 20 micron | 14.1 | 34.6 | 50.0 | 18.6 | 29.3 | 11.6 | 7.9 | 90.3 | - | 82.2 | 98.1 |
| 10 micron | 19.0 | 39.5 | 66.5 | 22.9 | 34.4 | 16.0 | 10.9 | 90.8 | - | 84.5 | 98.7 |

a Separate screening of another portion of sample.

Representative data from the literature are presented in Table 3.5-3 and show the same types of variations in the analytical results as those observed in our study.

From the sizing standpoint, BOF dusts are extremely fine with the bulk of material reported to be 1 micron or less(18,19,20). Our particle size analyses are given in Table 3.5-4.

The very fine particle size of some of the residues (i.e., the fine dusts and sludges) and the difficulty of dewatering the sludges present some problems in the management and disposal of these wastes. Before reuse or even disposal, the dewatering and/or agglomeration of these residues is often the practice.

BOF operations produce substantial dust emissions, with reported values in the U.S. plants varying from 8 kg/ton of product to 30 kg/ton. The eight plants we visited collected an average of roughly 20 kg of dust and sludge (dry basis) per ton of steel product (Table 3.5-5). In these works, almost 90% of the collected residue is in sludge form with the balance in dust.

Table 3.5-5 BOF SLUDGE AND DUST COLLECTIONS - 1974

| Plant | Residue Collected - % Steel Prod. | | |
|---|---|---|---|
| | Sludge[a] | Dust | Total |
| A | 2.0 | - | 2.0 |
| D | 0.6 | 1.4 | 2.0 |
| E | 0.5 | 0.2 | 0.8 |
| F | - | 2.5 | 2.5 |
| G | 3.0 | - | 3.0 |
| I | 2.0 | - | 2.0 |
| J | 1.8 | - | 1.8 |
| K | 1.5 | - | 1.5 |
| Weighted Avg. | 1.79 | 0.22 | 2.0 |

[a] Dry basis

The method of BOF residue disposal for the eight steel works with BOF operations is presented in Table 3.5-6. Of the residues, 24.3% is recycled via the sinter strand, 50.2% is landfilled, and 25.5% is stocked.

Table 3.5-6 BOF RESIDUE DISPOSITION - 1974

| Plant | Disposition |
|---|---|
| A | Landfill |
| D | Landfill |
| E | Recycle - sinter |
| F | 50% recycled/ sale - 50% stock |
| G | Landfill |
| I | Stocked |
| J | Recycle - sinter |
| K | Stocked |

Summation: Weighted Average

| | |
|---|---|
| Landfill | 50.2% |
| Recycle | 24.3% |
| Stock | 25.5% |

The main problem in recycling of the BOF pollution abatement residues is the tramp element content (mainly zinc and lead) and to a lesser extent, the fine consistency of the BOF pollution control residues. (For details on problems of recycling, see Section 3.16, Recycling.)

Based on information obtained in England, Germany and Japan and from data in the literature(2,4,5,10,11,14,17) the chemical composition and size distribution(19) of the fines in other countries are essentially the same as in the U.S. The quantities of residues collected from the BOF operations are also very similar (Table 3.5-7).

Table 3.5-7 QUANTITIES OF BOF POLLUTION CONTROL RESIDUES COLLECTED BY COUNTRIES
(kg/ton of steel)

| | |
|---|---|
| United States | 8 - 30 |
| England | 14 - 20 |
| Germany | 13 - 30 |
| Japan | 11 - 25 |

The quantities in the U.S. vary between 8 and 30 kg/ton of steel produced, while in the other three countries, with high steel production, the quantities are between 11 and 30 kg/ton.

For the collection of the residues abroad, "wet" pollution control devices are usually used. Even in Germany and Japan where earlier "dry" systems were used to a significant extent, the trend today is toward scrubbing (mostly in venturi-type scrubbers) and toward wet electrostatic precipitators. However, even in some of their most modern facilities, dry electrostatic precipitators are still used by the Japanese. Baghouses are also used in Japan to control the BOF "fugitive emissions."

In Japan the recovery of BTU values from the BOF off-gases, especially since the energy crises, is becoming popular. For instance, in one steel works, the ICR (IRSID, France), systems are used but their newest furnace utilizes the Bischoff (German) gas recovery system.

An international study(19) gives somewhat higher figures (30-33 kg/ton) for particulates generated in BOF operations (Table 3.10-8).

Table 3.5-8 RAW RESIDUAL LOADS ASSOCIATED WITH BOF STEEL MANUFACTURING PROCESSES(19)

| Type of Discharge | Raw Residual Load (kg/ton of steel) |
|---|---|
| BOF - Airborne | |
| Particulates | 30.0 - 33.0 |
| BOF (Semi-wet) Waterborne | |
| Suspended solids | 0.5 |
| Fluoride | 0.04 |
| pH | 10 - 12 |
| BOF (Wet) Waterborne | |
| Suspended solids | 5.0 |
| Fluoride | 0.08 |
| pH | 6 - 9 |

Presently about 41% of the BOF residues are recycled in England while the goal is toward 100% recycling in Germany and Japan. The Germans have developed the Berzelius-Lurgi variations of the Waelz process and the SL/RN process, and the Japanese, the Kawasaki process. The Japanese, using partly the German-American SL/RN and the Kawasaki processes, are already recycling even the zinc and lead-containing residues, and in Germany the Berzelius-Lurgi plant has been in operation since 1974. The BSC has completed a feasibility study and has considered building a recycling unit capable of handling Zn and Pb-containing BOF and other residues(17).

## 3.5 REFERENCES - BASIC OXYGEN FURNACE

1) The Making, Shaping and Treating of Steel - Ninth Edition, United States Steel Corporation, 1971.

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3) Brinn, D. G. A Survey of the Published Literature Dealing with Steel Industry In-Plant Fines and Recycling. NTIS, PB-236,359, 1974.

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## 3.6 SUBCATEGORY: OPEN HEARTH FURNACE (OH)

The conversion of molten iron to steel is accomplished in one of three furnace types: open hearth (OH), basic oxygen (BOF), or electric (EAF). At one time most of the steel produced in this country was made in open hearth shops but their popularity has been falling rapidly since the introduction of BOF steel making(1). Table 3.6-1 shows the extent of the decline of the importance of OH in the production of steel(2).

Table 3.6-1 PERCENT OF RAW STEEL PRODUCED BY FURNACE TYPE

| Furnace Type | Percent of U.S. Production 1974 | 1969 | 1964 |
|---|---|---|---|
| Open hearth | 24.3 | 43.1 | 77.3 |
| Basic oxygen | 56.0 | 42.6 | 12.2 |
| Electric | 19.7 | 14.3 | 9.9 |
| Other | - | - | 0.6 |
| Total % | 100.0 | 100.0 | 100.0 |
| Raw steel produced in 100,000 tons | 145.7 | 141.3 | 127.1 |

There have been no new OH facilities built in this country in recent years and based on information obtained from the steel companies there are no plans to construct new ones in the future, since both the BOF and EAF offer savings in time and energy costs. As a result, the open hearth method of producing steel will continue to decline in importance as the older furnaces are taken out of service.

The open hearth furnace is a shallow, rectangular, covered hearth. A charge is evenly distributed on the refractory hearth and heated by passing hot burning gases over the materials from alternate ends of the furnace. In a normal regenerative operation checker chambers are used for heat recuperation. Oxygen is usually added through roof lances to increase flame temperatures and heat transfer after the hot metal was added to the hearth. This is done to reduce a normal charge-to-tap time of 10 hours to 7-8 hours(1).

Firing time is largely dependent on the size and makeup of the charge which, in theory but not in normal practice, can vary from all hot metal to all scrap. The charge composition depends upon the relative availabilities of hot metal and in-plant or purchased scrap, with typical scrap usage in the 45 - 55% range. The solid components are charged first. These will normally be scrap and/or cold pig iron, fluxing agents (limestone or lime primarily) and raw ore, briquettes, sinter or nodules as a source of reaction oxygen. At the proper time and with partial melting of the solids, the molten iron is introduced. Then, after several distinct reaction phases within the bed and a final refining period, during which most of the C and S are removed from the melt, the charge is ready to tap.

In 1970 there were 408 basic open hearth furnaces in the United States in operation, with capacities ranging from 30 to 600 tons/heat(1). This included a small number of tilt-type furnaces that were or had been previously used in duplexing operations. Also 10 acid open hearths still in operation were reported(1). Open hearth steel production in 1970 was 48,022,000 tons whereas in 1974 only 35,499,000 tons of OH steel were produced(2), confirming the continuing decline in the usage and availability of these units.

The four plants we visited with OH shop operations had a total of 25 OH furnaces in 1974 with capacities ranging from 240 tons/heat to 335 tons. Operating fuels for these units varied from oil and tar to natural and by-product gases.

Cleaning of the off gases from furnace operations is the major and only source of pollution abatement residues in typical OH steelmaking practice. Because of the nature of the charge and the variety of firing fuels, these gases usually contain not only entrapped particulates but also combustion as well as reaction products. Wet and dry gas cleaning systems are used. If wet, venturi scrubbers are standard; if dry, dry electrostatic precipitators are used.

Since the four shops we visited all had dry cleaning systems and a dust residue, we were not able to obtain first-hand information relative to wet collection systems. However, it is reported(3) that the aqueous discharge from wet scrubbers is treated the same as in BOF practice except that pH adjustment has to be made because of the acidic nature of the discharged wastes. This same source describes two such systems, both of which use water recycle and blowdown. Coagulation aids are needed(4) to settle the solids because of the fineness of the suspended particles.

Our chemical analysis of the dust samples obtained for this study are given in Table 3.6-2. The iron content of the dusts varies from 34.4 - 65.7%. The tramp element content such as zinc varied from less then 0.05 to as high as 26.6%, lead from 0.07 to 2.0%, and the $Na_2O + K_2O$ content from 0.67 to 3.15%. Similar variation in the chemical composition of the OH residues is shown in the data presented in the literature (Table 3.6-3).

The results of our sample screenings, particle size analysis, are presented in Table 3.6-4, indicating that all open hearth dusts are of very fine consistency. According to one source in the literature(6) 50% of the OH fines are below 5 microns in the U.S. A paper on Czech OH practices indicates that 70% of the dust particles are below 1 micron(10).

Of the three major steelmaking processes (OH, BOF, and EAF), the open hearth process produces the smallest amount of pollution control residue on a kg-per-ton-of-raw-steel-produced-basis. The four operations we observed had a weighed average of collected dust equivalent to 1.1% (11 kg/ton) of steel produced (Table 3.6-5). Similar quantities of

OH dusts generated (e.g., 10 kg/ton(11) or 4.2 kg/ton without oxygen lancing and 4.7-11 kg with oxygen lancing(19)) were reported in the literature. However, it should be noted that the quantities generated depend not only on the processing practices but also on the composition of the raw material feed. For instance, if a high ratio of scrap with high zinc and lead content is used, quantities of dusts collected also increase (since essentially all of these volatile metals are expelled during the steelmaking).

None of the four plants indicated that they were directly recycling any of their dusts at the time of our visit. One plant was selling its waste to an associated outside concern for non-steel use. Another was stockpiling in anticipation of the startup of a briquetting facility which would handle this as well as other fine plant wastes. Presumably these briquettes would then be recycled within the plant as furnace feed. The remaining two installations sent their dust to landfill sites. Overall, we found that 58% of the dust was landfilled, 29% stocked, and 13% sold. Obviously, this small sampling has distorted the true industry-wide picture since the sale of these residues is minimal according to most authorities on the subject.

In Germany in 1974 there were no pollution controls on open hearth furnaces and, therefore, no residues were collected. As late as 1975, during our visit to Germany, only one experimental open hearth off-gas dedusting system was in operation, but the residue quantities collected with this experimental electrostatic precipitator were not available.

According to the OECD, ED study 2-20 kg airborne and 5 kg waterborne residues are generated in open hearth operations(14) (Table 3.6-6). In Japan only 1.3% of the raw steel produced during 1974 was made in open hearth furnaces(12). Since it is regarded as a negligable problem by the Japanese steel industry and the Environment Agency of Japan, the only information obtained on this subject was the typical chemical analysis of OH residues (see Table 3.6-3, reference 15) from the

Environment Agency.

In England "only certain" OH furnaces have dust control equipment on the off-gases. The quantities of residues collected are relatively small (i.e., less than 5% of all of the dust collected in the iron and steelmaking furnace operations). In the British Steel Corporation facilities, 26,000 tons of OH residues are collected of which none are recycled. Of this 26,000 tons, 4,000 (or 15%) are sold and 22,000 (or 85%) are dumped(13).

In the U.S., based on the information obtained from the four plants which had OH operations, as stated before, 87% of the OH residues are dumped or stocked and 13% sold. Based on additional information obtained during our study, less than 20% of the OH residues were sold or recycled in the U.S. in 1974.

The main problems in the recycling of these residues are (1) the high tramp element content, especially zinc and lead, and (2) the very fine consistency of the dusts.

For further details on problems of recycling OH residues, see Section 3.16, Recycling.

Table 3.6-2 CHEMICAL ANALYSES OF OPEN HEARTH DUSTS
(weight %)

| Plant | Sample | Fe | C | S | Pb | Sn | Zn | Mn | $Na_2O$ | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ | As | Sb | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | 62.0 | 0.3 | 1.1 | 0.6 | 0.09 | 2.0 | 0.18 | 0.23 | 1.8 | 0.15 | 1.2 | 0.32 | 0.7 | <0.02 | <0.01 | <0.01 |
| | 2 | 58.3 | 0.3 | 1.2 | 1.4 | 0.10 | 3.5 | 0.20 | 0.43 | 2.1 | 0.13 | 0.83 | 0.27 | | | | |
| | 3 | 58.8 | 0.5 | 1.0 | 1.2 | 0.06 | 4.8 | 0.16 | 0.36 | 2.3 | 0.11 | 0.95 | 0.37 | | | | |
| | 4 | 55.5 | 0.3 | 1.3 | 1.6 | 0.10 | 5.8 | 0.12 | 0.50 | 2.1 | 0.13 | 0.87 | 0.27 | | | | |
| F | 1 | 64.3 | 0.5 | 1.2 | 0.14 | <0.01 | 0.23 | 0.07 | 0.35 | 0.73 | 0.15 | 0.74 | 0.28 | 0.5 | <0.02 | <0.01 | <0.01 |
| | 2 | 65.2 | 0.4 | 0.76 | 0.07 | <0.01 | 0.18 | 0.06 | 0.27 | 0.54 | 0.11 | 0.92 | 0.27 | | | | |
| G | 1 | 49.7 | 0.4 | 1.3 | 2.0 | 0.12 | 10.5 | 0.11 | 0.44 | 2.5 | 0.19 | 0.93 | 0.48 | 0.5 | <0.03 | <0.01 | <0.01 |
| | 2 | 34.4 | 0.3 | 0.93 | 1.3 | 0.10 | 26.6 | 0.02 | 0.47 | 2.1 | 0.17 | 0.48 | 0.22 | | | | |
| | 3 | 48.6 | 0.3 | 0.99 | 1.9 | 0.13 | 12.0 | 0.19 | 0.85 | 2.3 | 0.26 | 0.97 | 0.70 | | | | |
| | 4 | 46.3 | 0.4 | 0.20 | 1.5 | 0.10 | 16.6 | 0.07 | 0.43 | 2.1 | 0.19 | 0.46 | 0.23 | | | | |
| H | 1 | 64.7 | 1.2 | 0.46 | 0.46 | 0.02 | 0.07 | 0.38 | 0.16 | 0.71 | 0.45 | 2.6 | 0.90 | 0.8 | <0.02 | <0.01 | <0.01 |
| | 2 | 64.2 | 0.5 | 0.11 | 0.83 | 0.02 | 0.07 | 0.16 | 0.15 | 0.52 | 0.17 | 1.2 | 0.41 | | | | |
| | 3 | 64.7 | 0.4 | 0.61 | 0.52 | 0.03 | 0.33 | 0.17 | 0.20 | 0.59 | 0.11 | 0.82 | 0.40 | | | | |
| | 4 | 65.7 | 0.7 | 0.51 | 0.35 | 0.02 | 0.03 | 0.12 | 0.13 | 0.83 | 0.04 | 0.50 | 0.20 | | | | |

NOTE: All samples are from dry ESP.

Table 3.6-3 CHEMICAL ANALYSES OF OPEN HEARTH RESIDUES (from Literature)
(weight % dry basis)

| Reference | Fe | C | S | Pb | Zn | Mn | Alkalies | $Al_2O_3$ | CaO | MgO | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 66.0 | 0.64 | 0.55 | 0.12 | 3.0 | 0.35 | - | 0.25 | 0.94 | 0.4 | 1.1 |
| 6 | 55.0 | - |  | 0.8 | 5.0 | 0.3 | - | - | - | - | - |
| 7 | 50.5 | - | 1.1 | 0.8 | 15.1 | 0.2 | - | 0.2 | 0.7 | 0.3 | 0.6 |
| 8[a] | 63.5/<br>68.0 | - | 0.34/<br>0.70 | 0.05/<br>0.95 | 0.21/<br>1.64 | - | - | - | - | - | - |
| 9[a] | 55.9/<br>63.7 | - | 0.40/<br>2.7 | 0.50 | 0.56/<br>1.7 | 0.47/<br>0.49 | 0.47/<br>0.49 | 0.4/<br>0.67 | 0.85/<br>1.06 | 0.39/<br>1.86 | 0.4/<br>0.92 |
| 13 | 27-51 | - | - | 1.8-2.5 | 8-10 | - | 2 | - | - | - | - |
| 15 | 65.1 | - | 0.2 | - | 1.2 | - | - | - | 0.6 | - | 0.7 |
| 15 | 64.7 | - | 0.1 | - | 1.4 | - | - | - | 1.6 | - | 0.3 |

[a] Range of results reported by the authors.

Table 3.6-5 PARTICLE SIZE ANALYSES OF OPEN HEARTH DUSTS

(Cumulative Percent Retained on Screen)

| Screen | Plant |  |  |  |
|---|---|---|---|---|
|  | C | F | G | H |
| 30 mesh | T | - | - | - |
| 50 mesh | 0.1% | - | - | - |
| 100 | 1.0 | - | - | - |
| 200 mesh | 8.3 | - | - | - |
| 325 mesh | 22.8 | - | - | - |
| 325 mesh [a] | 21.2 | 8.4% | 5.0% | 3.6% |
| 20 micron | 42.7 | 18.5 | 12.4 | 8.6 |
| 10 micron | 57.9 | 24.9 | 15.2 | 12.6 |

[a] Separate screening of another portion of sample.

Table 3.6-5 QUANTITIES OF RESIDUES GENERATED IN OPEN HEARTH STEELMAKING OPERATIONS

| Plant | Residues Collected % of Raw Steel |
|---|---|
| C | 1.0 |
| F | 0.6 |
| G | 1.2 |
| H | 2.0 |
| Weighted Avg. | 1.1 |

Table 3.6-6 RAW RESIDUAL LOADS ASSOCIATED WITH THE OPEN HEARTH STEEL MANUFACTURING PROCESSES(14)

| Type of Discharge | Raw Residual Load (kg/ton of steel) |
|---|---|
| OHF - Airborne | |
| Particulates | 2.0 - 20.0 |
| $SO_2$ | 0.7 - 6.0 |
| OHF (Wet) - Waterborne | |
| Suspended solids | 5.0 |
| Fluoride | 0.05 |
| Nitrate | 0.09 |
| Zinc | 1.0 |
| (pH) | (3 - 7) |

## 3.6 REFERENCES - OPEN HEARTH FURNACES

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## 3.7 SUBCATEGORY: ELECTRIC ARC FURNACE (EAF)

As the phasing out of the basic open hearth process has progressed in recent years, the use of the electric arc furnace has increased. This type of furnace, once considered primarily for alloy steel production, accounted for almost 20% of the U.S. steel output in 1974 with over 65% of this in carbon steel grades(1). Part of its increasing popularity is due to the fact that it can be used to produce the full range of steels starting with a cold charge of scrap and/or pig iron. Since it needs no hot metal, this furnace lends itself to those smaller plants where basic iron production facilities are either limited or lacking altogether. Because of its versatility, it is used to supplement BOF operations in many of the larger integrated plants.

The electric arc furnace consists of a refractory-lined cylindrical steel shell and dished bottom with a large shell diameter-to-depth ratio. Since most modern furnaces use top charging, a refractory-lined, removable top is standard. This top has three openings through which retractable graphite electrodes are inserted. Heat to melt and process the charge is produced by the electrical arcing between the electrodes and the charge as well as the passage of the current through the bath(2).

The furnaces are mounted on rocking mechanisms so that they can be tilted backwards for slag removal and forwards for tapping. Doors or covered ports in the shell provide for observation, fettling, oxygen or other gas refining, and for fluxing and alloying material additions. Mechanical or magnetic induction stirrers are normally used to agitate the bath and assure better mixing and blending.

After charging of the scrap and fluxing agents, which may take more than one charge/melt cycle, the melting and refining proceed. Slag control is the important consideration in the EAF process, and the fact that slags can be easily adjusted to meet a wide variety of operating conditions accounts for the inherent flexibility of the process. Whether a single or double-slag approach is used, an oxidizing slag is provided for the meltdown period followed by a reducing slag for refining. Oxygen lancing during the oxidizing period shortens the process time to roughly two to four hours(11). When bath chemistries reach the desired end points, the heat is tapped.

The U.S. EAF production in 1974 was 28.7 million tons(1) and the four plants which had EAF facilities of the eleven plants we visited produced almost 2.4 million tons of steel during the same period in electric arc furnaces.

Electric arc furnaces come in a wide range of sizes, from under 5 tons per heat to over 300 tons. Four of the plants we visited had EAF facilities; their 13 furnaces ranged in size from 20 tons/heat to 165 tons. All plants but one had blast furnaces to produce iron for the EAF's.

Wet, semi-wet and dry collection systems are used to control fume emissions from EAF's. The wet systems use venturi scrubbers; the semi-wet, precipitators or baghouses in conjunction with "wet" spark or spray chambers; the dry, primarily baghouses. Process waste water effluents from the wet and semi-wet systems are clarified in much the same way as they are in the BOF circuits, resulting in a sludge or dewatered filter cake for disposal.

Three of the four plants in this study used baghouses. The fourth has furnace evacuation systems and venturi scrubbers (they are in the process of adding a baghouse for shop dust and fume control). The water circuit here is a closed loop with a small bleed. Included in the loop are thickeners, chemical addition (if needed), cooling tower and vacuum filters. This same circuit handles waste waters from their continuous casting and vacuum degassing units.

Table 3.7-1 CHEMICAL ANALYSES OF EAF RESIDUES
(weight % dry basis)

| Plant | Sample | Fe | C | S | Pb | Sn | Zn | Mn | $Na_2O$ | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ | As | Sb | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Dust[a] | | | | | | | | | | | | | | | | |
| | 1 | 39.1 | 1.6 | 0.23 | 0.14 | 0.09 | 0.31 | 2.2 | 0.32 | 2.4 | 0.66 | 8.87 | 4.6 | 4.5 | 0.02 | <0.01 | <0.01 |
| | 2 | 35.0 | 1.6 | 0.16 | 0.14 | 0.09 | 0.28 | 1.4 | 0.31 | 2.3 | 0.72 | 11.8 | 6.9 | | | | |
| C | Dust[a] | | | | | | | | | | | | | | | | |
| | 1 | 33.5 | 0.5 | 0.29 | 3.4 | 0.07 | 15.1 | 1.8 | 0.64 | 2.8 | 0.38 | 6.31 | 2.8 | 3.0 | 0.02 | <0.01 | <0.01 |
| | 2 | 31.8 | 0.6 | 0.03 | 3.9 | 0.07 | 15.2 | 1.6 | 0.23 | 3.2 | 0.36 | 6.34 | 2.8 | | | | |
| H | Dust[a] | | | | | | | | | | | | | | | | |
| | 1 | 30.6 | 0.9 | 0.24 | 1.8 | 0.05 | 4.5 | 3.3 | 0.32 | 1.1 | 0.49 | 20.9 | 2.3 | 3.5 | 0.02 | <0.01 | <0.01 |
| | 2 | 25.0 | 0.7 | 0.21 | 1.6 | 0.03 | 6.1 | 1.1 | 0.55 | 1.1 | 0.41 | 29.0 | 2.0 | | | | |
| | 3 | 32.0 | 0.5 | 0.24 | 1.7 | 0.06 | 5.2 | 1.8 | 0.32 | 1.4 | 0.76 | 22.1 | 2.5 | | | | |
| | 4 | 23.9 | 0.6 | 0.22 | 3.4 | 0.07 | 6.4 | 2.1 | 0.57 | 1.7 | 0.68 | 5.57 | 2.2 | | | | |
| M | Sludge[b] | | | | | | | | | | | | | | | | |
| | 1 | 21.7 | 3.1 | 0.06 | 0.42 | 0.08 | 1.6 | 1.2 | 0.05 | 0.14 | 0.30 | 30.2 | 1.6 | 1.9 | 0.02 | <0.01 | <0.01 |
| | 2 | 37.0 | 0.5 | 0.05 | 0.18 | 0.03 | 1.1 | 0.9 | 0.05 | 0.18 | 0.40 | 6.9 | 1.0 | | | | |
| | 3 | 40.6 | 2.5 | 0.11 | 0.07 | <0.01 | 0.17 | 1.5 | 0.06 | 0.12 | 0.43 | 15.4 | 1.5 | | | | |
| | 4 | 33.3 | 3.6 | 0.15 | 0.34 | <0.01 | 1.4 | 1.0 | 0.09 | 0.17 | 0.26 | 19.6 | 1.2 | | | | |

[a] Baghouse

[b] Filter cake

Table 3.7-2 CHEMICAL ANALYSES OF EAF RESIDUES (FROM LITERATURE)
(weight % dry basis)

| Plant | Sample | Fe | C | S | Pb | Sn | Zn | Mn | $Na_2O$ | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $3^a$ | | 33.1 | 1.4 | 0.62 | 0.92 | 0.01 | 4.8 | 3.9 | - | - | 1.9 | 15.7 | 7.8 | 0.12 |
| $3^a$ | | 33.6 | 0.48 | 0.45 | 0.84 | 0.003 | 1.4 | 3.8 | - | - | 2.9 | 17.2 | 5.9 | 0.10 |
| $4^b$ | | 34.0 | - | 0.49 | 1.5 | - | 7.4 | - | - | - | - | 6.1 | - | 4.6 |
| (A) $4^b$ | | 29.0 | - | - | 2.0 | - | 16.0 | 4.0 | - | - | - | - | - | - |
| (R) $5^b$ | | 21.7/<br>34.9 | 0.1/<br>7.4 | - | 0.6/<br>2.7 | - | 0.9/<br>5.2 | 2.6/<br>6.4 | 0.5/<br>4.1 | - | 0.4/<br>4.2 | 0.6/<br>7.4 | 0.7/<br>8.8 | - |
| (R) $5^c$ | | 21.8/<br>53.9 | - | - | Trace/<br>2.7 | - | Trace/<br>5.0 | 0.5/<br>3.3 | - | - | - | - | - | - |
| (R) $6^d$ | | 30.0/<br>40.0 | 0.5/<br>0.9 | 0.2/<br>0.3 | - | - | 2.5/<br>7.0 | 4.6 | - | - | - | 10.8/<br>18.0 | - | 3.0/<br>4.0 |
| (R) $7^d$ | | 28.5/<br>55.8 | 0.7 | 0.2/<br>1.0 | 0.1/<br>5.1 | | 4.7/<br>9.5 | 3.8/<br>3.9 | | 0.1/<br>2.2 | 0.3/<br>1.2 | 1.9/<br>10.5 | 0.6/<br>4.1 | 1.9/<br>4.6 |
| $8^c$ | | 33.2 | 0.30 | 0.48 | 2.6 | | 24.8 | 3.3 | 0.5 | | 0.8 | 1.3 | 0.4 | 3.4 |

a Raw fume b Dust c Wastes d Fines (A) Average (R) Range

Chemical analyses of the three dusts and one joint treatment sludge from these four plants are given in Table 3.7-1. The iron values in the EAF residues we obtained and analyzed range between 21.7 and 40.6% (total Fe). The tramp element content, such as zinc, varied between 0.17 to 15.2%, the lead content between 0.07-3.9%, and the $Na_2O + K_2O$ content between 0.19 and 3.4%. The high tramp element contents, in most cases, make the direct recycling of these residues through conventional agglomeration processes impractical.

EAF pollution abatement residue analyses from other sources are given in Table 3.7-2. As expected, these data obtained from the literature (since they represent a greater variation of EAF steelmaking practices) show even a greater variation in chemical composition than those we have obtained from four steel mills in the U.S. Respectively, the total iron contents vary from 21.7 to 53.9%, the zinc content from trace to 24.8%, and the lead content from trace to 2.7%.

The following table (Table 3.7-3) lists the results of our screen analysis of the three dusts and the additional sludge samples to which we had access:

Table 3.7-3 PARTICLE SIZE ANALYSES OF EAF RESIDUES

| | | Screen Sizing | | |
|---|---|---|---|---|
| Plant | Fines | -10 microns | -20 microns | -325 mesh (44 microns) |
| G | Dust | 79.6% | 84.8% | 94.3% |
| H | Dust | 76.4 | 83.9 | 93.4 |
| A | Dust | 70.1 | 78.5 | 89.6 |
| M | Sludge | 68.6 | 73.0 | 84.5 |

These results are somewhat coarser than those reported in a review article on the "steel industry in-plant fines"(7).

The quantities of residues collected at the various sites are presented in Table 3.7-4.

Table 3.7-4 QUANTITIES OF RESIDUES GENERATED

IN EAF OPERATIONS

| Plant | Residue | % of Steel Production |
|---|---|---|
| A | Dust | 0.9 |
| B | Sludge [a] | 1.2 |
| C | Dust | 1.6 |
| H | Dust | 1.4 |
|  | Weighted Avg. | 1.3 |

[a] Includes continuous casting and vacuum degassing residues.

These values are in line with data given in the literature(7,9,10) and all are within the range of roughly 0.3 to 2.0% reported in a recent international study(11). The airborne and waterborne residues generated in electric arc furnace operations are presented in Table 3.7-5 based on the aforementioned study.

Because of the limited sampling available to us, the figures we developed relative to the disposal techniques in the plants we visited may not be representative. We found that 56% of the collected residues are disposed of as landfill, 38.4% was stocked and 5.6% recycled. The stocking is being done at only one plant in anticipation of an on-site recovery process in the construction stage at the time of our visit. The small percentage recycled was said to be going back to the electric arc furnaces.

Table 3.7-5 RAW RESIDUAL LOADS ASSOCIATED WITH EAF STEEL MANUFACTURING PROCESS (11)

| Type of Discharge | Raw Residual Load (kg/ton of steel) |
|---|---|
| EAF - Airborne | |
| Particulates | 3.0 - 20.0 |
| EAF (Semi-wet) - Waterborne | |
| Suspended solids | 0.8 |
| Fluoride | 0.01 |
| pH | 6 - 9 |
| EAF (Wet) - Waterborne | |
| Suspended solids | 3.5 |
| Fluoride | 0.02 |
| Zinc | 0.02 |
| pH | 6 - 9 |

The electric arc furnace operations in England, Germany and Japan also have pollution control facilities. As in the U.S., both "wet" and "dry" collection systems are used. The quantities of residues generated in the different countries represent a wider range than the quantities generated in the U.S. alone. The data obtained in Europe fall between 5-20 kg/ton of raw steel and in Japan between 3.6-10 kg/ton. However, the Japanese pointed out that when scrap high in zinc (and lead) is used in combination with high scrap ratios, significantly higher quantities (20-25 kg) of residue per ton of steel can occasionally be generated.

Because of the high tramp element content (zinc and lead), all of the EAF residues in England are dumped(2). The 49,000 tons* of EAF residues generated per year contain 6,500 tons of zinc and 1,500 tons of lead.

In Germany and Japan the residues are either recycled or stored. In both countries special installations are used for the processing and recovery of metal values from these wastes, and there are plans for building a similar installation in England. For further details on recycling, see Section 3.16, Recycling.

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* From BSC operations: The private sector contributes about 10% of the total tonnage of steel produced in England.

## 3.7 REFERENCES - ELECTRIC ARC FURNACE

1) Annual Statistical Report for 1974. American Iron and Steel Institute, Washington, D. C., 1975.

2) The Making, Shaping and Treating of Steel - Ninth Edition. United States Steel Corporation, 1971.

3) Hopkins, D. W., Johnson, W., and Davies, R. Constitution of Oxide Fume from Steelmaking Ironmaking & Steelmaking Quarterly (British Steel Corporation) No. 1, 1974, pp. 25-29.

4) Barnard, P. G., et al. Recycling of Steelmaking Dusts. In: Proceedings of 34th Mineral Waste Utilization Symposium, Chicago, 1972, pp. 63-68.

5) Powell, H. E., Dressel, W. M., and Crosby, R. L. Experimental Metals Reclamation Process Recovers Alloys from Steel Mill Wastes. 33 Magazine, Vol. 13 (4), April 1974, pp. 48-50.

6) Cavaghan, N. J., and Traice, F. B. Utilization of In-Plant Fines. JISI 208 (6), 1970, pp. 538-42.

7) Brinn, D. G. A Survey of the Published Literature Dealing with Steel Industry In-Plant Fines and Their Recycling. U.S. Bureau Of Mines NTIS PB-236-359, August 1974.

8) Dressel, W. M., Barnard, P. G., and Fine, M. M. Pre-Reduced Pellets from Iron and Steelmaking Wastes. (Presented at AIME Annual Meeting, Chicago, 1973, Prepring #73-B-72, U.S. Bureau of Mines), pp. 12.

9) Lund, H. F. Industrial Pollution Control Handbook. McGraw-Hill Book Company, New York, 1971.

10) Trace Pollutant Emissions from the Processing of Metallic Ores. U.S. EPA, Washington, D. C., EPA 650/2-74-115, October 1974.

11) Organization for Economic Cooperation and Development, Environment Directorate (Preliminary Draft), PCC/AEU/ENV/74.2, Paris, 1975.

12) British Steel Corporation. The Arisings and Treatment of BSC In-Plant Fines. Swinden Laboratories, Moorgate, Rotherham, 1975.

## 3.8 SUBCATEGORY: VACUUM DEGASSING

Degassing under high vacuum is a technique used to adjust the final chemistry of steel in that period between tapping of the steelmaking furnace and the commitment to either ingot or various steel casting operations. This treatment effectively reduces hydrogen, oxygen and carbon levels while at the same time permits alloying element refinements(1). The net effect is cleaner steel with enhanced physical properties.

Based on often contradictory industry estimates, 5-8% of the steel produced in the United States was vacuum degassed in 1974. Most of the vacuum degassing was made in connection with continuous casting or large-piece steel casting operations.

While there are broad variations in means and equipment used for vacuum degassing, they all fall under three rather broad classifications:

1. Stream degassing,
2. Ladle degassing, and
3. Recirculation degassing.

In all cases, either the process itself or supplementary means (induction stirring or gas injection) are used to expose as much of the steel surface as possible to the vacuum during the roughly one-half hour degassing cycle. Superheating of the steel to 35-70° C above normal furnace tapping temperatures is also a common practice. This step, combined with preheating of the various vessels and equipment used and/or providing auxiliary heat during the cycle, helps to make up for heat losses during degassing and prevents premature skull formations.

In recent years, a new vacuum steelmaking technology, the VAR (vacuum-arc-remelting) process was developed and can be added to the list of vacuum steelmaking approaches. VAR is usually used for the manufacture of high strength and alloy steels.

Vacuum degassing systems range in capabilities from under one ton per charge to over 300 tons. Vacuums in the 300-1000 micron pressure range are required in the more common systems. These low pressures are achieved with multi-stage steam ejectors. Condensed steam and water from the barometric condenser, combined with exhaust gases are the normal process wastes from this operation. The liquid wastes will contain solid and dissolved constituents and the gaseous phase, some particulates and polluting gases.

Three of the eleven plants we visited had vacuum degassing facilities. None reported any separate air pollution control residues for vacuum degassing. Two of the three had water recycle systems. In these facilities the residues (suspended solids) contained in the process waters were removed in joint treatment facilities. The third facility had a once-through water system with the water undergoing joint treatment in deep bed filters with other process waters.

Since the residues from the vacuum degassing operations were not collected separately (in the plants we visited), we were neither able to collect samples for analyses, nor obtain information on the quantities collected. However, it may be noted that the quantities of residue collected from this operation are "very small." However, according to the OECD Study(2), the quantity can vary from 0.1 to 16.0 kg/ton of steel vacuum degassed.

According to information obtained through private communications(3), the chemical composition will vary with the type of steel degassed. In some cases, besides the low iron levels, high manganese levels were reported(4).

Neither in Europe (England and Germany) nor in Japan were the technical institutions, government agencies and the steel mill personnel able to supply information on the quantities or chemical composition of the vacuum degassing residues. The reason for this lack of information was the same as in the U.S.: (1) the quantities of residues generated are insignificant in comparison with other steelmaking or ironmaking pollution control residues; (2) the residues are not collected separately but treated jointly with other steelmaking residues, and (3) there are no significant quantities of tramp elements in these residues.

## 3.8 REFERENCES - VACUUM DEGASSING

1) The Making, Shaping and Treating of Steel - Ninth Edition. United States Steel Corporation, 1971.

2) Organization for Economic Cooperation and Development. Environment Directorate, PCC/AEU/ENV/75.2 (Preliminary Draft), Paris, August 1975.

3) Unpublished data. Dravo Corporation Research Center.

4) Varga, J., Jr., and Lonnie, H. W. A Final Technological Report on a Systems Analysis Study of the Integrated Iron and Steel Industry. Battelle Memorial Institute, Columbus, Ohio.

## 3.9 SUBCATEGORY: CONTINUOUS CASTING (CC)

One of the newer technologies for casting steel is continuous casting. This is a one-step operation whereby molten steel is directly converted to a semi-finished shape (slab, bloom, billet or, in some instances to a strip or round) suitable for direct processing in secondary rolling operations. This approach supplants and offers some distinct economic and operating advantages over the conventional teeming, ingot stripping, soaking pit, preheating and primary rolling operations(1). In 1974 approximately 12% of the raw steel produced in the U.S. was continuously cast(2).

In practice, molten steel is poured from the ladle into a tundish, an intermediate pouring container, and thence into the top of an open-ended, water-cooled cooper mold. This mold is of square, oblong or round cross-section in line with the desired shape of the product to be cast. As the molten metal solidifies, it is drawn out of the bottom of the mold by and through roll sets and high pressure cooling water sprays. Hot metal input, roll speeds and water spray rates are all inter-controlled so that a continuous flow of solidified and shaped steel product is achieved. Depending on the type of caster, the circuit may also contain straightening rolls as well as a sizing roll stand(s) to provide considerable versatility as to final product dimensioning. This "endless" ribbon of steel then enters a cut-off station where it is mechanically or flame-cut into convenient working lengths.

Air pollution is not a major problem in a continuous casting shop, being largely limited to emissions during pouring and cut-off. However, substantial quantities of water are required and some of this does pick up solids (scale) and oil. In addition, many continuous casting shops use one or more closed or semi-closed loop circuits for either or both of their contact (process) and non-contact waters in which case the cleaning of the non-contact waters add to or results in sludge which is attributable to the operation.

Three of the plants we visited had continuous casting facilities in operation in 1974 and were able to provide some data as to the pollution control residues from these facilities. One additional mill had a new continuous casting installation at the time of our visit with insufficient data available for our study. The three plants from which operating data were received are discussed in the following paragraphs.

Plant B - One closed loop water system (with blowdown) is used to provide water for their electric furnace, vacuum degassing and continuous casting shops. This circuit contains scale pits, chemical additive tanks, thickeners and a cooling tower. The underflow from the thickeners is vacuum filtered and the filter cake is landfilled. The continuous casting shop is served by its own scale pit and the amount of scale collected here is a little over 0.6% of the quantity of steel continuously cast. This scale is sold as BF feed.

Plant G - This plant has both slab and billet casting facilities. Process water for the slabbing unit is closed circuit with bleed. The circuit includes a scale pit, cooling tower, filters and a clarifier. The non-contact water for this slab operation is also closed loop with a cooling tower and bleed to the process water system. The resultant pollution control wastes are scale and sludge for the slab caster.

Contact and non-contact waters for the billet caster are closed loop with the non-contact EAF water. This circuit consists of a scale pit, sand filters and cooling tower. Scale and sludge result.

The total quantity of scale collected from both casting operations amount to about 0.2% of the steel tonnage cast and is a negligible amount (0.03%) of the total steel production at this plant. The combined output of sludge is only 105 tons/year - again an insignificant residue. The scale is "stocked" and the sludge landfilled.

Plant K - Their multi-strand casting unit is served by two water circuits - one open and one closed. The closed loop (presumably the non-contact) water circuit contains flat and deep bed filters which yield only a very small amount of sludge (185 tons/year). On the other hand, the scale collected in the open contact water circuit comes to about 2.5% of the total steel cast (roughly 0.3% of the steel produced at this plant). The sludge is landfilled and the scale recycled.

In the English and German steel works no data were available on the quantities of residues, scale or sludge produced. In Japan 2.6 kg of scale is generated per ton of steel cast. "Small quantities" of oil containing sludge and scum are also generated in their casting operations, but the quantities are not measured because they are jointly treated with the other oily wastes, in their "oily waste disposal facilities" and with the other sludges in their sludge treatment facilities. An OECD study(3) gives data on the raw residual loads generated in continuous casting operations (Table 3.9-1).

Table 3.9-1 RAW RESIDUAL LOADS ASSOCIATED WITH CONTINUOUS CASTING (3)

| Type of Discharge | Raw Residual Load (kg/ton of steel) |
|---|---|
| Airborne residuals | |
| Particulates | NA |
| Waterborne residuals | |
| Effluent flow (lit./ton) | (17,514) |
| Suspended solids | 0.9 |
| Oil and grease | 0.5 |
| (pH) | (6 - 9) |

This study places the quantity of suspended solids at 0.9 kg/ton of steel cast, in the process water, indicating again that the sludge portion of the continuous casting residues is very small.

The collected scale is always directly recycled without further treatment either through their plant, furnace operations, or through sintering. The sludges and scums are also usually recycled but only after they undergo one of the two previously mentioned waste treatment and an additional agglomeration, mostly sintering, operation.

## 3.9 REFERENCES - CONTINUOUS CASTING

1) The Making, Shaping and Treating of Steel - Ninth Edition. United States Steel Corporation, 1971.

2) Anonymous. Worldwide Continuous Casting Roundup - Part III. 33 Magazine, December 1975, pp. 42-47. (Calculated from information contained in this article.)

3) Organization for Economic Cooperation and Development. Environment Directorate, PCC/AEU/ENV/75.2 (Preliminary Draft), Paris, 1975.

## 3.10 SUBCATEGORY: ROLLING

Most of the steel produced in the open hearth, basic oxygen and electric arc furnaces is tapped into refractory-lined ladles and then "teemed" into cast iron molds to form ingots. However, today, especially in more modern plants, the trend is toward continuous casting of billets, slabs and blooms. It is during this period from furnace to ingot (or before continuous casting) that any final refining steps such as chemistry adjustments and vacuum degassing are completed(1). After partial or complete cooling, the mold is stripped from the ingot and the ingot is placed in "soaking pits" for reheating(and heat treating) in preparation for subsequent processing steps.

Ingots can vary widely in shape and weight depending, to a large extent, on the end product desired and the rolling equipment available. Weights, for example, can go from several hundred pounds (speciality steels) to several hundred tons (large forgings). Most ingots, however, fall in the 10 to 40 ton range and are intended for the production of the vast quantities of mass-produced steel products that are needed in our industrial society.

These products are made by passing the ingot through a succession of pressurized rolls and forming operations which slowly and inexorably reduce the cross-sectional area of the ingot to the final or near-final shapes and forms desired. Most of this is done hot, followed, in some cases, by further reduction in "cold rolling" mills. Many integrated plants have associated specialized finishing mills which are generally considered as part of their rolling operations since they are, in many cases, integral with or natural continuations of their rolling operations. Examples of the latter are pipe mills using semi-finished "skelp" or billets as feedstock and wire and nail mills which reduce rod stock to marketable finished products. Pickling and plating processes which may also fall under the latter were considered as separate subcategories for the purposes of this study.

Although some steel is hot-rolled from ingot to final form in one continuous operation, the normal approach is to do this in at least two distinct steps. The first step in the conversion process is the rolling of heated ingots into one of three intermediate shapes: slabs, blooms or billets. Slabs are rectangular in cross section and are intended for further rolling to plate or sheet. Blooms and the slightly smaller billets are essentially square or oblong sections of lesser cross-sectional areas than the slab. These pieces end up, for example, as rails and structural shapes (blooms) or bars, rounds and wire (billets).

After cooling, the blooms, billets and slabs are generally referred to as semi-finished steel. At this time, they undergo "conditioning" which is nothing more than a thorough inspection followed by chipping, scarfing and/or grinding to remove surface imperfections which might affect the quality of the finished steel product. After the conditioning, the semi-finished steel is ready for further hot working by rolling or forging, coupled, in some cases, with cold working operations that follow the secondary hot working. These final forming and finishing operations are performed in a wide variety of mills normally designated by some name descriptive of the operation being done, i.e., hot plate mill, rod mill, bar mill, structural mill, etc. (These designations are often prefixed with a sizing number in inches, which roughly describes the roll stand used.) Interspersed throughout these facilities are the secondary operations, such as tempering, annealing and leveling, which are required to impart certain physical and new metallurgical qualities to the final steel products.

In 1974 almost 110 million tons of steel products were shipped which underwent usually more than one rolling operation before leaving the mills. Table 3.10-1 shows the various steel products and the quantities shipped in 1974.

Table 3.10-1 SHIPMENTS OF STEEL PRODUCTS - 1974(2)

(ALL GRADES, INCLUDING CARBON, ALLOY

AND STAINLESS)

| Product | Tons |
|---|---|
| Semi-finished | 5,509,284 |
| Shapes and plates | 18,128,323 |
| Rails and accessories | 1.785,391 |
| Bars and tool steel | 18,514,292 |
| Pipe and tubing | 9,843,661 |
| Wire and wire products | 3,171,387 |
| Sheets and strip | 44,991,065 |
| Tin mill products | 7,528,166 |
| TOTAL net shipments | 109,471,569 |

Although rolling or hot/cold forming are basic and sizeable operations at most steel plants, these operations produce only a minor quantity of airborne pollution. Most of this arises from the scarfing, grinding and other surface preparation steps entailed in the conditioning of the steel during its conversion from ingot to finished form. On the other hand, rolling requires large quantities of water for roll and material cooling, scale removal and flushing purposes. These waters do become contaminated with oil and suspended solids.

From an air quality standpoint, six plants reported on fume and dust collection residues at various conditioning steps. Table 3.10-2 summarizes this information.

While hot and cold rolling operations are similar, their liquid wastes are different and are usually handled separately. There are a number of reasons for this but basically they center around the fact that in cold rolling, various oils and emulsions are used and cold rolling shops are generally contiguous with other cold finishing operations (plating, pickling, etc.) that require more extensive waste water treatment than that normally afforded hot mill effluents.

Table 3.10-2 RESIDUES COLLECTED IN ROLLING AIR POLLUTION CONTROL FACILITIES

| Plant | Operation | Collection Equipment | Collected Residue |  | Location and Comments |
|---|---|---|---|---|---|
|  |  |  | Nature | Quant. % of Steel Produc. |  |
| A | Scarfing | Wet ESP | Sludge | Negligible | Slab mill |
|  | Grinding | Baghouse | Dust | 0.1 | Conditioning bldg. |
| B | Grinder | Mechanical collector | Dust | 0.6 | Slab mill |
|  | Grinder | Mechanical collector | Dust | 0.1 | Stainless steel finishing mill |
| C | Scarfing | Mechanical collector | Sludge | Unknown | Slab mill - residue with scale |
| F | Scarfing | Wet EPS | Sludge | Unknown | Joint treatment |
| H | Grinder | Baghouse | Dust | 0.1 | Billet mill |
|  | Grit blast | Baghouse | Dust | 0.1 | Blooming mill |
| I | Scarfing | Wet scrubber | Sludge | Unknown | Slab mill - residue collected with scale |

Hot rolling and forming generate large quantities of iron-bearing residues. These wastes, mainly scale and fine iron oxides, are flushed out of the various mills along with the process waters used for descaling, roll and material cooling and other purposes. The minimum treatment provided consists of settling out the heavier and larger suspended solids (scale) in adjacent scale pits or settling basins before discharging the overflow. While some of the entrained oil adheres to and is removed periodically with the scale, most of the oil is skimmed or drawn from the water surface using one of many devices that can be attached to the pits for that purpose. The overflow from these pits then goes on to subsequent treatment facilities where additional oil and the finer solids are removed.

Table 3.10-3 lists the various hot mill water circuits used at the eleven plants in our study. All had hot rolling operations although only ten had cold forming shops. As noted, two of the plants provided no treatment other than scale pits. Two plants had water recycle systems and three others had similar loops on at least some of their mills. In summary, all of the plants had scale pits and collected their scale; four plants had their own individual treatment facilities for final processing of their hot mill waste waters while five used joint waste water treatment plants.

Table 3.10-3 WASTE PROCESS WATER TREATMENTS FOR HOT ROLLING OPERATIONS

| | | | | Water Treatment Facilities | | | | | Residue Coll. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Water Recycle | | | Scale Pit | Settl. Ponds or Basins | Clarif./ Thicken. | Chem. Addit. | Sand/ Bed Filters | Scale | Sludge or Filter Cake |
| Plant | Yes | No | Partial | | | | | | | |
| A | | X | | X | | | | | X | - |
| B | X | | | X | X | X | X | | X | J |
| C | | X | | X | | | | | X | - |
| D | | X | | X | X | | | | X | X |
| E | | | X | X | X | | | | X | X |
| F | X | | | X | X | X | | | X | X |
| G | | | X | X | X | X | | | X | J |
| H | | X | | X | | X | X | X | X | J |
| I | | X | | X | X | X | X | | X | J |
| J | | | X | X | | X | | X | X | X[a] |
| K | | X | | X | X | | | | X | J |

NOTE: "J" denotes "joint residue"  a Joint with scale

The total quantity of rolling residues is estimated to be approximately 7.4 million tons in 1974(3). Of this, less than 200,000 tons is estimated to originate from the cold rolling operations, leaving a balance of roughly 7.2 million tons for the hot rolling (and conditioning) residues.

Liquid wastes from cold rolling operations differ in two respects from those generated by hot rolling. They contain little, if any, scale or iron-bearing particulate but they are more heavily ladened with oil and rolling emulsions. Consequently, scale pits are generally not necessary in cold mill water circuits, but the emphasis is placed on oil removal. Five of the ten plants we visited had closed, roll lubricating fluid loops for all or some of their mills. Such circuits not only conserve valuable lubricating compounds but also limit the amount of spent oil and gook that must be discharged to the waste process water system for subsequent treatment. The total quantity of "pollutants removed" in the cold rolling operations of the U.S. steel industry was estimated to be 148,600 tons in 1973(4).

In all cases but one, cold mill aqueous wastes were treated jointly with other waste waters, usually those from associated pickling and plating operations. The exception was a closed loop water system with waste water bleed discharge to a municipal treatment system after a de-emulsifying operation to recover the oils. All of the others put their joint wastes through settling stages (clarifiers or thickeners) and/or filters (sand or deep bed) and/or lagoons. In six of the nine instances, chemical additions were used to break up the emulsions and to separate the solids.

The oil and oily sludges collected here as well as that collected in the other treatment facilities throughout the plants were disposed of in one of the following ways:

1) Used internally as tramp oil (road beds, dust suppressors, miscellaneous fuels, etc.) or donated to outsiders.

2) Reprocessed within the plant for reuse as fuel oil or lubricant.
3) Sold to outsiders for reprocessing.

The chemistry of pollution control residues resulting from rolling operations would be expected to vary widely although basically dependent on the steel grades being worked. Reuse of these wastes is highly desirable since they are normally high in iron content and low in tramp metallic elements such as lead and zinc. However, they sometimes contain deleterious oil and grease residuals which can and do often preclude direct recycling through sintering operations.

We used the basic sample data originally supplied for this study through the AISI and supplemented this information with some additional analyses (mainly total iron and oil/grease). During our plant visits we also obtained some samples which we also analyzed. The data and information gathered from these sources has been broken down into the following categories which fairly well represent the three types of rolling mill residues presently collected in the mills:

1) Conditioning residues - grinder and scarfing dusts or sludges.
2) Scale - collected from scale pits or primary settling basins.
3) Scale/sludge - resulting from secondary treatment of scale pit aqueous effluents.

Table 3.10-4 presents the chemical data on conditioning residues from four of the plants studied. Samples A, B, C and D, for example, represent composite weekly samples taken over a four-week span and the numbered sample analyses are individual day samples arbitrarily selected from the weekly samples. Some sizeable variations in steel types being rolled over these periods are obvious.

The quantities of scale collected in the scale pits at the various plants varied considerably (i.e., between 18 and 102 kg/ton of steel rolled (Table 3.10-5). The iron contents of the scale are high (57.7 -

Table 3.10-4 CHEMICAL ANALYSES OF STEEL CONDITIONING RESIDUES
(weight %)

| Plant | Sample | Fe | Zn | Pb | Sn | Al | Cu | K | Cr | Mn | Ni | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Grinder Dust A | | <.001 | <.001 | | | .013 | | .098 | .63 | .033 | Conditioning shop |
| | B | | .004 | <.001 | | | .016 | | .370 | .61 | .32 | |
| B | Grinder Dust A | | .002 | <.001 | | | .16 | | 4.2 | 1.20 | 3.0 | Slab mill |
| | B | | .003 | <.001 | | | .17 | | 12.5 | 1.05 | 7.0 | |
| | C | | .002 | <.001 | | | .16 | | 10.0 | 1.05 | 6.3 | |
| | D | | .002 | <.001 | | | .13 | | 1.3 | 1.32 | 0.9 | |
| | Grinder Dust 1 | 73.2 | .004 | .004 | | 1.18 | 0.05 | .004 | | | | Slab mill |
| | 2 | 57.1 | .007 | .006 | | 0.42 | 0.23 | .080 | | | | |
| | 3 | 72.0 | .004 | .004 | | 0.90 | 0.09 | .020 | | | | |
| | 4 | 88.8 | .002 | .004 | | 0.08 | 0.08 | .120 | | | | |
| | Grinder Dust C | | <.001 | <.001 | | | .05 | | 3.75 | .23 | 2.7 | Alloy processing |
| C | Grinder Waste | | | | | | | | | | | |
| | A | | .085 | .002 | | | .034 | | .005 | .150 | .016 | |
| | B | | .140 | .002 | | | .047 | | .008 | .180 | .019 | |
| | C | | .310 | .002 | | | .037 | | .007 | .127 | .018 | High oil |
| | D | | .140 | .002 | | | .049 | | .008 | .150 | .025 | Content sludge |
| H | Grinder Dust A | | .005 | .013 | | | .185 | | .300 | .550 | .434 | Conditioning shops |
| | B | | .003 | .005 | | | .040 | | .002 | .130 | .030 | |
| | C | | .005 | .006 | | | .100 | | .120 | .120 | .090 | |
| | D | | .002 | .004 | | | .055 | | .077 | 1.010 | .075 | |

(continued on next page)

Table 3.10-4 CHEMICAL ANALYSES OF STEEL CONDITIONING RESIDUES (continued)
(weight %)

| Plant | Sample | Fe | Zn | Pb | Sn | Al | Cu | K | Cr | Mn | Ni | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | Grit Blast | | | | | | | | | | | |
| | Dust A | | .005 | .005 | | | .200 | | .130 | .860 | .080 | Conditioning shops |
| | B | | .004 | .003 | | | .050 | | .001 | .016 | .020 | |
| | C | | .004 | .004 | | | .075 | | .090 | .600 | .075 | |
| | D | | .005 | .001 | | | .050 | | .003 | .300 | .030 | |
| | Grinder Dusts | | | | | | | | | | | |
| | 1 | 68.4 | .004 | .010 | .02 | .11 | .10 | .010 | | | | Conditioning shops |
| | 2 | 63.9 | .004 | .020 | .06 | .11 | .09 | .010 | | | | |
| | 3 | 69.2 | .006 | .020 | .03 | .10 | .08 | .010 | | | | |
| | 4 | 70.3 | .003 | .030 | .02 | .07 | .06 | .006 | | | | |
| | 5 | 78.5 | .006 | .006 | .04 | .04 | .06 | .006 | | | | |
| | 6 | 77.8 | .006 | .008 | .03 | .04 | .06 | .010 | | | | |

NOTES: Lettered samples (A, B, etc.) are composite and consecutive weekly samples.

(Analyses performed by Calspan Corporation)

Numbered samples (1, 2, etc.) are individual day samples taken from the lettered weekly samples (A, B, etc.).

Table 3.10-5 SCALE COLLECTION AND DISPOSITION

| Plant | Scale as % of Total Steel Production | Disposition |
|---|---|---|
| A | 1.6 | Recycle - BF |
| B | 1.8 | Sold for BF and sinter |
| C | 5.8 | Recycle - sinter |
| D | 4.8 | Recycle - BF and sinter |
| E | 2.6 | Recycle - BF and sinter |
| F | 7.0 | 50% stock/50% sold or sinter |
| G | 5.3 | Stock |
| H | 3.3 | 25% recycle/75% stock |
| I | 10.2 | Recycle - sinter |
| J | 8.2 | Recycle |
| K | 3.9 | Recycle - sinter |
| **Weighted Avg.** | 5.1 | |

| Disposition summary: | | |
|---|---|---|
| | Recycle | 69.6% |
| | Stock | 29.7 |
| | Sale | 0.7 |

81.9%) and oil and grease levels generally lie in the 0.1 to 1.9% range (Table 3.10-6a). Results obtained from the literature show similar variations in iron content (Table 3.10-6b).

Table 3.10-6a IRON AND OIL CONTENT OF ROLLING MILL SCALES
(weight %)

| Plant | Mill | No. Samples | Total Fe | Oil |
|---|---|---|---|---|
| A | Primary | 2 | 68.8 - 70.0 | .01 - 1.0 |
| B | Slab | 1 | 64.3 | 0.1 |
|  | Hot strip | 2 | 67.5 - 71.5 | .09 - 1.9 |
| C | Blooming | 2 | 77.5 - 81.9 | 0.1 |
| G | Structural | 5 | 61.2 - 74.0 | 0.1 - 0.6 |
| I | Plate | 6 | 60.2 - 72.9 | 0.1 - 0.8 |
|  | Hot strip | 5 | 73.5 - 74.9 | 0.1 - 0.3 |
| J | Primary | 2 | 57.7 - 68.8 | - |
| K | Hot strip | 2 | 73.1 - 74.8 | 0.2 |
|  | Blooming | 2 | 66.1 - 71.7 | 0.2 - 0.5 |

Rolling mill sludges resulting from treatment of the scale pit effluent waters in two of the four plants visited not using joint treatment means were examined and the results are given in Table 3.10-7. Iron levels are somewhat lower, but oil/grease contents are substantially higher than in scales. In both cases, these residues are landfilled.

The quantities of conditioning wastes generated in rolling operations have been previously given in Table 3.10-2. Although these data are somewhat meager, it would appear that these wastes would constitute no more than 1 or 2% of the total quantity of waste generated at most plants if they are collected separately and not included with scale figures. Scale collections, on the other hand, can be quite sizeable (Table 3.10-5) with rather a large spread between the low and high percentages.

Table 3.10-6b CHEMICAL ANALYSES OF ROLLING MILL SCALES (FROM THE LITERATURE)
(weight %)

| Ref. | Fe | C | S | Pb | Zn | Mn | NagO | $K_2O$ | $Al_2O_3$ | CaO | MgO | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 63.0 | - | 2.0 | 0.002 | 0.004 | - | - | - | 1.9 | 3.8 | - | - |
| 6 | 73.9 | - | - | 0.001 | 0.005 | 0.72 | - | - | 0.50 | 0.65 | 0.72 | 0.55 |
| 7 | 73.0 | 1.2 | - | - | - | - | - | - | - | - | - | - |
| (R) 8 | 73.0/<br>74.0 | 0.5/<br>0.7 | 0.02/<br>0.1 | - | - | - | - | - |  | 0.2/<br>1.8 | 0.2 | 0.4/<br>1.9 |
| (R) 9 | 62.6/<br>73.7 | 0.01/<br>0.16 | 0.01/<br>0.16 | 0.004/<br>0.014 | 0.003/<br>0.007 | - | - | 0.01/<br>0.019 | 0.5/<br>2.2 | 0.1/<br>3.4 | 0.3/<br>1.1 | 0.2/<br>3.4 |
| 10 | 73.7 | 0.8 | 0.03 | - | - | - | - | - | 1.7 | 0.1 | - | 0.6 |
| 11 | 72.3 | - | 0.04 | - | - | - | - | - | - | 0.8 | 0.2 | 0.5 |
| (R)12 | 54.3/<br>75.4 | 0.05/<br>7.11 | - | 0.00/<br>0.04 | 0.00/<br>0.05 |  | 0.01/<br>0.09 | 0.01/<br>0.09 | - | - | - | - |

(R) Range of all the results reported by the authors.

Table 3.10-7 CHEMICAL ANALYSES OF HOT ROLLING MILL SLUDGES
(weight % dry basis)

| Plant | Sample | Fe | Zn | Pb | Sn | Al | Cu | K | Cr | Mn | Ni | F | Oil | Mill |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| J | A | - | .040 | .009 | | | .015 | | .016 | .230 | .025 | .009 | | Hot strip |
| | B | - | .033 | .004 | | | .013 | | .013 | .180 | .020 | .004 | | |
| | C | - | .036 | .004 | | | .014 | | .014 | .185 | .021 | .004 | | |
| | D | - | .036 | .008 | | | .014 | | .014 | .179 | .020 | .008 | | |
| | 1 | 72.5 | .12 | .005 | .015 | .11 | .01 | - | | | | | 11.4 | Hot strip |
| | 2 | 72.5 | .07 | .006 | .013 | .18 | .01 | - | | | | | 10.0 | |
| | 3 | 70.3 | .10 | .010 | .013 | .88 | .01 | - | | | | | 11.9 | |
| | 4 | 61.0 | .11 | .011 | .011 | .47 | .01 | - | | | | | 12.2 | |
| F | 1 | 66.2 | .009 | .01 | - | .003 | .003 | .12 | | | | | 7.4 | Primary |
| | 2 | 64.9 | .01 | .008 | .03 | .02 | .02 | .11 | | | | | 13.9 | |
| | 1 | 69.7 | .01 | .02 | .13 | .01 | .01 | .01 | | | | | 30.4 | Hot strip |
| | 2 | 65.9 | .08 | .03 | .12 | .03 | .03 | .10 | | | | | 33.1 | |

NOTE: Lettered samples (A, B, etc.) are composite and consecutive weekly samples analyzed by Calspan Corporation. Numbered samples are our analyses of day samples from the weekly lettered samples, in the case of Plant J, and are samples we obtained in the case of Plant F.

The quantities of sludges generated from waste water treatment, attributable to rolling operations, is difficult to discern, since six of the nine plants have joint facilities or, as in one case, combine these residues with their scale as an integral part of their treatment circuits. The information we were able to gather is given below (Table 3.1-8).

Table 3.10-8 QUANTITIES OF ROLLING MILL SLUDGES GENERATED AND THEIR DISPOSAL

| Plant | Mill(s) | Sludge (% of Scale Collected) | Disposition |
|---|---|---|---|
| D | All | 5 | Recycle - sinter |
| E | All | 24 | Landfill |
| G | All | 8 | 50/50 (landfill/ stock) |
| J | Hot strip | 25 | Landfill |

Two of the six shops providing information on their conditioning residues dispose of them as landfill, with the balance reporting reuse with their scale. Roughly 70% of the scale is recycled to the sinter plant or hot melt facilities; slightly less than 30% is stocked for future recovery or dumped and less than 1% is sold. As noted above (Table 3.10-8), only a small portion of the generated sludge is reused at present.

In Europe and Japan, essentially the same pollution control methods are used in the treatment of hot and cold rolling wastes and effluents as in the U.S. Scale pits, oil skimmers and clarifiers in combination with chemical treatment are typical for hot rolling operations. However, large settling basins and/or ponds are also employed in some cases as a final residue removal step. The clarified water is recycled almost without exception.

While scale pits are seldom found in cold rolling operations, so-called "buffer pits" are. The small amounts of settled solids from these pits are usually handled jointly with the sludges generated in the related subsequent treatment steps where emulsion breakers and flocculants are used.

In most cases, the oily waste residues from the skimmers and emulsion breaking operations are sent to special waste oil treatment facilities where the oils are recovered either for their original application (i.e., rolling lubricant) or for fuel. In some cases, the waste oil and scum is sold to, and the oil and fats recovered by, an outside contractor. Some mills in Japan use their scum in their in-plant incinerators as a fuel to help burn their rubbish.

The quantities of scale and sludge generated in the rolling operations of the various countries differ somewhat (Table 3.10-9).

Table 3.10-9 QUANTITIES OF RESIDUES GENERATED IN ROLLING OPERATIONS BY COUNTRIES

| | kg/ton of Raw Steel | |
|---|---|---|
| | Scale [a] | Sludge |
| United States | 16 - 102 | 0.1 - 1.9 |
| Germany | 15 - 75[b] | 1 - 2 |
| England | 22 - 58 | 2 - 3 |
| Japan | 26 - 40[c] | 0.3 - 1 |

[a] Including conditioning residues.

[b] Kg/ton of rolled steel.

[c] Based only on the data obtained from Japan's three largest (all >10 million tons/year capacity) mills, producing large % heavy gage steels.

The residual loads associated with the hot and cold rolling operations, based on a recent international study(13), are presented in Table 3.10-10.

As in the U.S., the larger-sized particles (>5 mm in England, >8 mm in Germany) are recycled directly through the blast furnace operations and the exceptionally large particles (>50 mm) through steelmaking furnaces, while the fines (<5 mm) are recycled through sintering operations. In the three large Japanese mills, all rolling mill residues are recycled through sintering.

While in the U.S., 69.6% is recycled (and 0.7% sold)[*], in England 87%, in Germany 95-98%, and in Japan almost 100% is recycled. The balance in England and Germany, as in the U.S., is usually "stored," with the exception of some oily sludges which are dumped. (In Japan the dumping of oily sludges in most districts where the steel mills are located is not permitted and, therefore, after an extra de-oiling treatment, even these fines are recycled.)

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[*] Based only on information obtained from the 11 mills visited during our study.

Table 3.10-10 RAW RESIDUAL LOADS ASSOCIATED WITH THE HOT ROLLING AND COLD FINISHING OPERATIONS(13)

| Type of Discharge | Raw Residual Load (kg/ton) | |
|---|---|---|
| | Hot Rolling | Cold Finish. |
| Airborne residuals | | |
| Particulates | 0.4 - 3.5 | 3.0 - 7.0 |
| Sulfur dioxide | 1.0 - 4.0 | - |
| Aerosols | - | 2.0 - 4.0 |
| Waterborne residuals | | |
| Primary breakdown mill and cold rolling | | |
| (effluent flow, lit./ton) | (4,090) | |
| Suspended solids | 2.0 | 0.5 - 1.5 |
| Oils and emulsions | 0.5 | 0.8 - 1.2 |
| Pipe and tubing mill | | |
| (effluent flow, lit./ton) | (10,000) | |
| Suspended solids | 3.5 | |
| Oils and emulsions | 0.7 | |
| Plate mill | | |
| (effluent flow, lit./ton) | (9,175) | |
| Suspended solids | 3.0 | |
| Oils and emulsion | 0.6 | |
| Bar mill | | |
| (effluent flow, lit./ton) | (15,000) | |
| Suspended solids | 3.5 | |
| Oils and emulsions | 0.7 | |
| Wire and wire products mill | | |
| (effluent flow, lit./ton) | (10,000) | |
| Suspended solids | 3.5 | |
| Oils and emulsions | 0.7 | |
| Hot rolled sheet mill | | |
| (effluent flow, lit./ton) | (40,000) | |
| Suspended solids | 4.1 | |
| Oils and emulsions | 0.8 | |

## 3.10 REFERENCES - ROLLING

1) The Making, Shaping and Treating of Steel - Ninth Edition. United States Steel Corporation, 1971.

2) Annual Statistical Report for 1974. American Iron and Steel Institute, Washington, D. C., 1975.

3) Pasztor, Laszlo. Problems of Resource Recovery in the Iron and Steel Industry. In: Proceedings of the Fourth Annual Industrial Pollution Conferences, WWEMA, Houston, Texas, March 1976.

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## 3.11 SUBCATEGORY: PICKLING

The hard, black oxide scale formed on the steel as a result of the basic hot-forming operations, including hot rolling, can be a troublesome problem and must be removed before many of the subsequent hot or cold finishing steps. This scale can adversely effect surface appearance, die and roll wear, dimensional uniformity, and the ability to coat and plate the steel. Pickling, the removal of scale (and in some cases of rust) through the use of acid solutions, is the operation universally employed in the mills to clean the surface of the steel before further or final processing of steel.

Pickling can be performed in various ways: from pure batch to semi- and continuous operations. In any event, the steel to be de-scaled (or surface activated) is first immersed in an acid bath(s) for some suitable period of time and then removed and subsequently washed or rinsed with water to remove the residual acid. The combination of acid bath(s) and rinse or post treatment stations constitute the essential elements of the industrial "pickle line."

The most commonly used acids are sulfuric($H_2SO_4$) and hydrochloric (HCL) with the latter being more popular in recent years(1). In use, they are diluted with water to levels which, in combination with a suitable operating temperature, provide the greatest acid activity. For example, 12 to 25% $H_2SO_4$ concentrations at 93-105°C (200-220° F.) in continuous pickling applications. Agitation of the bath with respect to the work, or vice versa, is generally used to optimize the pickling operation.

De-scaling during pickling and removal of rust is accomplished at the expense of the acid; the free acid content decreases with time and the build-up of metallic salts in the bath increase to such an extent that the pickling acid can no longer function efficiently. At this point, the acid must be replaced or replenished with a fresh solution and spent acid, commonly referred to as "pickle liquor," must be withdrawn from the system and disposed of. Similarly, the effectiveness of the wash/rinse solutions becomes impaired with times (usually because of increase in dissolved solids content and acidity) and they, too, must be replaced or replenished. As a consequence, the usual pickling operations (batch or continuous) result in two process waste effluents: spent pickle liquor and acidic rinse waters. Both can be difficult to dispose of. (However, in some cases, spent pickle liquor is used in municipal waste water treatment(15).)

Table 3.11-1 lists the various acids used in the pickling operations at the plants we visited, together with the disposition of their spent liquors. In-plant pollution control residues are generated at only three locations: Plants B, D, and K. Plant B treats their wastes acids along with their rinse water in a joint treatment facility. Details on this facility and the resultant waste are given in the discussion under subcategory 14, Waste Water Treatment Plants. The other two plants (D and K) have acid regeneration (HCl) systems that result in an iron oxide by-product. Plant D reports that this high purity oxide amounts to about 5 kg/ton of processed (pickled) steel. All but 6% of this 'waste" is sold, primarily to the magnetic tape industry. The unsold portion is landfilled because of high chloride content. Plant K did not have reliable figures available as to the quantity of oxide their regeneration operation produces but they sell all that they make.

In most of the plants where an actual pollution control residue results from the treatment of waste rinse waters, the resultant sludge is produced as a joint waste water treatment sludge (Table 3.11-2). These particular circuits are also covered under Subcategory 14, Waste Water Treatment Plants. Plant E has a wire mill pickle rinse water that is separately neutralized and settled, but their sludge is "impounded" at the same location as the sludge resulting from the joint treatment of their other waste rinse waters. Plant G uses a specially designed

Table 3.11-1 ACIDS USED AND METHODS OF SPENT LIQUOR DISPOSAL

| Plant | Acids Used | Disposal of Spent Liquor |
|---|---|---|
| A | $H_2SO_4$ | Neutralized/outside contractor/landfill |
| B | $H_2SO_4$, $HNO_3$, HF | Neutralized and lagooned/joint sludge to landfill |
| C | $H_2SO_4$ | Neutralized/outside contractor/landfill |
| D | HCL | Regeneration |
| E | $H_2SO_4$ , HCl | Reuse internally or deep well |
| F | $H_2SO_4$ | Outside contractor/conversion to $FeCL_3$ |
| G | $H_2SO_4$ , HCl | Deep well |
| H | $H_2SO_4$ | Outside contractor/deep well |
| I | HCl | Sold (for processing) or deep well |
| J | HCl | Slag pile |
| K | HCl | Regeneration |

Table 3.11-2 DISPOSITION OF WASTE PICKLING RINSE WATERS

| Plant | Disposition of Acid Wash/Rinse Waters |
|---|---|
| A | No information |
| B | Neutralized and lagooned/joint sludge to landfill |
| C | Neutralized and discharged to stream |
| D | Lagooned/joint sludge to landfill |
| E | Neutralization/clarification/joint impoundment |
| F | Neutralized/to municipal treatment plant |
| G | Deep well and lagooned/joint sludge to landfill |
| H | Chemical treatment/joint sludge to storage |
| I | Chemical treatment/joint sludge to storage |
| J | Neutralized/joint sludge to landfill |
| K | Neutralized/lagooned/joint sludge to landfill |

rinse water process on one of their pickling lines that greatly reduces the quantity of this water required. Consequently, they are able to dispose of the smaller amount of "bleed" from the system in the deep well where they also dispose of their waste liquor.

Typical chemical analysis of pickling sludges was reported by the In-Plant Fines Group of the British Steel Corporation(1) (Table 3.11-3).

Table 3.11-3 CHEMICAL ANALYSES OF PICKLE SLUDGE(1)

| Plant | Total Fe | C | Zn | Pb | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|
| 1 | 44.5 | 4.3 | 0.17 | 0.09 | 0.03 | 0.07 |
| 2 | 10.2 | 0.1 | 0.03 | 0.04 | 0.02 | 0.02 |
| 3 | 23.7 | 2.95 | 0.01 | 0.03 | 0.05 | .002 |

In Germany and Japan regeneration of the waste hydrochloric acids and recovery systems for used sulfuric acids are common practice. None of the mills in these two countries generated any pickling pollution control residues with the exception of small quantities arising in the rinse water neutralization operations.

In the acid regeneration processes iron oxide powder (from the hydrochloric acid regeneration) and the iron sulfate heptahydrate crystals (from the sulfuric acid recovery systems) are produced as by-products. In Japan one mill also produces iron chloride as a by-product. All of these by-products are sold. However, the iron oxides are balled and used as an ironmaking charge in the blast furnaces when, occasionally, the purity of the oxides do not meet customer specificiations. The only pickling residue dumped in Germany(3) and Japan(4) is part of the rinse water neutralization sludges. In some Japanese plants only 10% of the neutralization sludges are dumped while 90% are sold as raw material for cement manufacture(4).

In England where the regeneration of waste pickling acids is also gaining ground, the total quantity of pickling operation sludges at the British Steel Corporation is relatively small. It was estimated to be approximately 26,000 tons per annum, of which 41% was recycled, 34% sold and only 25% dumped or stocked for future recycling.

The various regeneration processes for sulfuric acid(6,7), hydrochloric acid(8,9,10,11,12), nitric-hydrofluroic acid(13,14), and waste pickling acids(5) will be briefly covered in Section 3.16, Recycling.

## 3.11 REFERENCES - PICKLING

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## 3.12 SUBCATEGORY: PLATING AND COATING

The utility of many basic steel products (sheets, strips, plates, wires, etc.) depends on the application of additional surface treatments, coating or plating. These surface treatments extend the life of the steel under conditions of storage, exposure to various environments and end-use, although aesthetic considerations are also often of considerable importance. Some of these supplementary treatments (galvanizing, tinning and chrome-plating, for example) are routinely associated with the finishing operations in the mills. Most of the mills covered in our study had one or more of these metallizing and/or similar coating operations.

According to the AISI Annual Statistical Report(1), of the 109,471,569 tons of "steel shipped in 1974," 5,549,389 tons (or 5.1%) was tin-coated, 6,105,109 tons (or 5.6%) galvanized (zinc-coated), and 997,759 tons (or 0.9%) received other metallic coatings. Smaller additional quantities received various chemical (and/or lubricating) coatings.

Both in the tinning and galvanizing operations, hot-dip and electrolytic coating methods are used. The tinning operations in the U.S. are overwhelmingly electrolytic, although in some foreign countries hot-dipped tin plating is still used to a considerable extent(2). On the other hand, the galvanizing (zinc plating) operations were almost 95% hot-dip operations in the U.S.(1) Tin and lead mixtures (usually 20% tin and 80% lead) are also used to coat steel sheets, producing so-called terne sheets ("long-terne sheets") and terne plates.

None of the mills we visited reported any pollution control residues as a result of their coating and plating facilities. The aqueous wastes from the cleaning and pickling ahead of the coating baths are handled as indicated in the discussion under Subcategory 3.11, Pickling. Sludges, dross and waste coating/plating solutions are considered to be process wastes as are those from any post-treatment operation used to provide special surface finishes. Most metal-bearing wastes are returned to the supplier for reprocessing and metal recovery, while some is still disposed as landfill. Other liquid wastes are generally handled along with the acid rinse waters from pickling or discharged directly to a lagoon or final treatment plant. The management and disposal of the residues from these operations was discussed in Subcategory 3.11, Pickling, or will be discussed in Subcategory 3.14, Waste Water Treatment Plants.

Neither in Europe nor in Japan were any of the iron and steel industry pollution control experts whom we had contact with aware of any residues arising in pollution control facilities of their metallic coating operations. The metal-containing process wastes either are sold or recycled by the metal suppliers. The process waters from the cleaning, including pickling operations, are usually jointly treated with the wastes from the pickling or rolling operations. In one Japanese coating operation, the oily effluents are treated in their "oil-containing waste-water disposal facility"(3) and after the removal of the oil and some suspended solids the water is recycled.

## 3.12 REFERENCES - PLATING AND COATING

1) Annual Statistical Report for 1974. American Iron and Steel Institute, Washington, D. C., 1975.

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## 3.13 SUBCATEGORY: BOILERHOUSES

Raw and finished steel production requires sizeable quantities of electric power. Traditionally, those steel plants containing blast furnace and coke forming operations have provided a part of their requirements with in-plant steam-powered generating facilities. Coke and blast furnace gases supplemented by oil, natural gas and coal have been the fuels used. Until recently, the trend had been away from coal in an effort to prevent undue air pollution, but with the new energy situation, the trend is reversed and it is expected that in the future more coal will again be used than in recent years.

Generating plants utilizing gaseous or liquid fuels yield essentially no solid residues unless they are treating their exhaust gases to remove $SO_2$. None of the plants in this study were doing so. Those plants using coal produce bottom ash or clinker which is, strictly speaking, a process waste, and fly ash which is usually a control residue since most plants have at least rudimentary collection systems to remove these particulates from their exhaust gas streams. Fly ash is high in silica and alumina with only a minor iron content of about 15% (dependent on coal used). As such, fly ash would not figure prominently, if at all, in any steel plant waste recovery system. Typical fly ash analyses are given in Table 3.13-1.

Only three of the visited plants reported one or more coal-burning boilers. All of these were equipped with dry centrifugal collectors of the multiclone or rotoclone type. The balance of the plants either specifically indicated no coal usage or no pollution control residues. Collected fly ash in all cases was combined with the bottom ash and disposed of as landfill.

The residues in flue gas desulfurization (FGD) are usually the Ca or Ca-Mg sulfite-sulfate type sludges (Table 3.13-2). In other systems (so-called recovery processes), in place of (throw-away) FGD sludges, by-products, such as elemental sulfur, gypsum, ammonium sulfate, or sulfuric acid, are produced in the pollution control facilities.

Table 3.13-1 CHEMICAL ANALYSES OF FLY ASHES FROM SOUTHWESTERN PENNSYLVANIA AREA (weight % - dry basis)

| | Range |
|---|---|
| CaO | 0.2 - 6.1 |
| MgO | 0.4 - 1.2 |
| Total sulfur | 0.1 - 1.8 |
| $SiO_2$ | 20 - 45 |
| $Al_2O_3$ | 16 - 40 |
| $Fe_2O_3$ | 8 - 33 |
| $Na_2O$ | 0.3 - 0.6 |
| $K_2O$ | 1 - 33 |
| $TiO_2$ | 1 - 2 |

The by-products are not considered as pollution control residues, neither in the iron and steel industry nor in the power generating industry.

The FGD sludges, if the fly ash is not removed prior to the $SO_2$ scrubbing, contain various quantities of fly ash besides the calcium (and magnesium) sulfite-sulfate precipitate, and, in some cases, limestone or "free lime."

The quantity of FGD sludge produced in the desulfurization of flue gases will depend on the sulfur content of the coal burned. For each percent of sulfur in the coal, approximately 40 kg/ton of coal (dry basis) or 80 kg/ton of coal sludge is produced(1), not counting the weight of the fly ash, that may be co-recovered with the sludge.

The disposal of the large quantities of FGD sludges generated, especially when coals with higher sulfur contents are burned, can be a problem because of the difficulties in the dewatering and the thixotropic properties of these sludges. However, at least two types of FGD sludge stabilization processes are already used in full scale power plant operations by the electric power generating industry. One of them is the Calcilox - Synearth(2,3) and the other the Poz-O-Tec process(4).

Table 3.13-2 CHEMICAL ANALYSES OF LIME AND LIMESTONE

FGD SLUDGES
(weight % - dry basis)

| | Lime | | Limestone | Lime | Limestone |
|---|---|---|---|---|---|
| | A[a] | B[a] | C[a] | D[b] | E[b] |
| CaO | 43.4 | 43.8 | 25.6 | 18.1 | 25.6 |
| MgO | .01 | | 1.2 | 2.4 | 1.2 |
| Total S | 20.0 | 22.9 | 8.4 | 7.2 | 10.9 |
| $SO_2$ | 29.2 | 45.8 | 11.6 | 12.1 | 10.8 |
| $SO_3$ | 13.6 | 0.0 | 6.4 | 2.9 | 13.6 |
| $CO_2$ | 7.1 | 1.0 | 30.0 | 3.2 | 2.2 |
| Free C | 2.8 | 0 | 1.8 | | .14 |
| $SiO_2$ | .58 | .18 | 1.4 | 31.6 | 21.3 |
| $Al_2O_3$ | 1.21 | .39 | .59 | 18.3 | 11.3 |
| $Fe_2O_3$ | .39 | .29 | .27 | 4.3 | 5.6 |
| $Na_2O$ | .35 | .09 | .52 | | .76 |
| $K_2O$ | .03 | 0 | .14 | | .98 |
| Free base as CaO | .06 | 0 | - | .3 | .06 |

a Fly ash removed prior to $SO_2$ scrubbing (A, B, C).

b Fly ash co-removed during $SO_2$ scrubbing (D, E).

## 3.13 REFERENCES - BOILERHOUSES

1) Pasztor, Laszlo, Selmeczi, J. G., and Labovitz, C. Stack Gas Desulfurization Residue Management. In: Proceedings of National Conference on Management & Disposal of Residues from Treatment of Waste Waters, Washington, D. C., February 1975.

2) Selmeczi, J. G., and Elnaggar, H. A. Properties and Stabilization of $SO_2$ Scrubbing Sludges. In: Proceedings of Coal and the Environment Meeting, National Coal Association, October 1974.

3) Calcilox for Sludge Stabilization. Dravo Lime Company Bulletin 75DL02-3M, Pittsburgh, Pa., 1975.

4) U.S. Congress, Committee on Interstate and Foreign Commerce. Hearings, Clean Air Act Amendments - Part 2. Serial No. 94-26, Washington, D. C., 1975.

## 3.14 SUBCATEGORY: WASTE WATER TREATMENT PLANTS

Most of the dry residues collected in iron and steelmaking plants are the results of air pollution controls and can, like many of the wet residues, usually be directly related to a specific iron or steelmaking operation, shop or facility. Some of the wet wastes, however, result from joint waste water treatment facilities (i.e., in which effluents from more than one steel mill operation are jointly treated). Therefore, it is difficult or impossible to assign these residues to any specific iron or steel mill operation. This heading (subcategory) was set up to cover and account for just such (mixed) pollution control residues.

All but two of the plants we visited had one or more waste water treatment plants that yielded residues that did not logically fall within the context of the various other subcategories in this study. These treatment facilities varied in complexity from nothing more than settling ponds or lagoons to one inter-connected series of three individual treatment systems feeding one final lagoon and producing but one common residue. Schematics of these treatment circuits as they were given or described to us are shown in Figures 3.14-I through 3.14-IX. These drawings may not be complete or factually correct in all instances since we emphasized the arising and management of the residues in our discussions of the various plants rather than the exact and sometimes proprietary means used to generate these wastes.

There are several things to be noted about these treatment plants. In all but one case they represent the final clarification step before the effluents are discharged from the plant or the water is reused. For another, the inputs are primarily finishing operation (coating, cold mill, pickling, etc.) waste waters combined with the secondary effluents from other plant treatment facilities such as settling tanks, clarifiers, etc., in the iron and steelmaking operations.

The chemistries of the sludges (Table 3.14-1) from these plants testify to the variety and nature of their inputs. Iron contents range from roughly 10% to a little over 40%. Oil contamination is high in all cases and this alone precludes recycling of these wastes in the normally practiced means without an intermediate oil removal step. Tramp element content, principally Zn, is also high in many instances, again making the recycling of these wastes through customary sintering operations impractical.

The quantities and dispostion of these sludges are given in Table 3.14-2. With the exception of Plant B, the amount of these wastes is not large compared to, say, scale or iron/steelmaking residues, but is significant in the overall picture. The rather substantial amount of Plant B sludge is due, as noted in the schematics, to the inclusion of all of the hot rolling process waters in this treatment plant.

Landfill is the predominant method of disposing of these wastes with six of the nine plants using this approach. Two plants stock these residues. The remaining plant recycles the "scale" portion of their waste (about 4% of their total scale collection) which is collected in scalping tanks while landfilling the remaining portion collected in the large settling tanks.

The waste water facilities in England, Germany and Japan are similar in several installations to those used in U.S. steel works. Most of the joint waste water treatment installations are serving more specific purposes than those described under the U.S. operations. In all three huge steel plants in Japan and in one works in Germany which we visited, special oily waste water treatment facilities are used for the removal of oil from the waste waters and slurries. In this way, the residues freed from oil became suitable for and are recycled. However, when no such special facilities are available, the waste water treatment plant residues are dumped or "stored" as in the U.S.

Table 3.14-1 CHEMISTRIES OF WASTE WATER TREATMENT PLANT SLUDGES
(Weight % - Dry Basis)

| Plant | Sample[a] | Zn | Pb | Sn | Al | Cu | K | Na | $SiO_2$ | Oil | Tot. Iron |
|---|---|---|---|---|---|---|---|---|---|---|---|
| B | B-1 | .081 | .003 | - | 0.29 | 0.02 | 0.03 | - | 2.48 | 3.4 | 16.0 |
| | | .049 | .003 | - | 0.26 | 0.03 | 0.07 | - | 1.96 | 9.8 | 25.1 |
| | B-2 | .011 | .007 | - | 0.50 | 0.02 | 0.04 | - | - | - | - |
| D | D-1 | 2.79 | 0.21 | 0.05 | 3.12 | - | 0.73 | - | - | 6.71 | 20.2 |
| | D-2 | 0.41 | 0.04 | - | 1.26 | - | 0.60 | - | - | 1.13 | 26.6 |
| E | E-1 | 0.40 | 0.01 | 0.07 | 0.88 | - | 0.73 | - | - | 14.9 | 15.3 |
| F | F-1 | 0.81 | 0.14 | 0.24 | 0.67 | 0.04 | 0.21 | - | - | 85.9 | 22.2 |
| | | 0.49 | 0.12 | 0.16 | 0.69 | 0.06 | 0.17 | - | - | 38.1 | 23.0 |
| H | H-1 | 0.75 | .040 | .040 | 0.67 | .020 | 0.45 | .020 | 4.89 | 3.9 | 34.0 |
| | | 0.92 | .053 | .035 | 0.77 | .026 | 0.47 | .017 | 5.65 | 4.5 | 39.7 |
| | | 0.96 | .051 | .039 | 0.59 | .035 | 0.36 | .018 | 5.11 | 6.2 | 43.2 |
| | | 0.12 | .063 | .035 | 0.73 | .042 | 0.44 | .016 | 5.70 | 8.0 | 43.4 |
| I | I-1 | .066 | .024 | .145 | 0.34 | 0.01 | - | - | - | 6.2 | 45.1 |
| | | .061 | .023 | .162 | 0.36 | 0.02 | - | - | - | 6.5 | 40.1 |
| | | .070 | .020 | .176 | 0.35 | 0.01 | - | - | - | 8.2 | 40.1 |
| | | .070 | .023 | .189 | 0.36 | 0.01 | - | - | - | 8.3 | 39.8 |
| J | J-1 | 1.80 | .010 | .019 | 3.07 | .005 | 51.3 | .008 | 2.09 | 16.5 | 37.5 |
| | | 1.27 | .013 | .019 | 2.13 | .006 | 50.4 | .013 | 3.29 | 26.0 | 38.6 |
| | | 3.51 | .011 | .020 | 3.32 | .004 | 60.2 | .011 | 2.97 | 15.9 | 32.0 |
| K | K-1 | Insufficient Samples | | | | | | | | | 10.7 |
| | | | | | | | | | | | 11.8 |
| | K-2 | 0.12 | .047 | 0.11 | 6.2 | - | 2.5 | .048 | 34.9 | 4.6 | 21.8 |

a Sample number refers to sample designations on respective waste water treatment plant schematics.

## Table 3.14-2 QUANTITIES AND DISPOSITION OF WASTE WATER TREATMENT PLANT SLUDGES

| Plant | Waste Sample No. | Nature of Waste | Quantity (as % of total steel produced) | Disposition |
|---|---|---|---|---|
| B | B-1 | Sludge | 2.6 | Landfill |
| | B-2 | Filter cake | 0.7 | Landfill |
| D | D-1 | Sludge | 0.4 | Landfill |
| E | E-1 | Filter cake | 0.6 | Landfill |
| F | F-1 | Oily sludge | 0.1 | Landfill |
| G | None | Scale | 0.20 | Recycle |
| | None | Sludge | 0.15 | Landfill |
| H | H-1 | Filter cake | 0.3 | Stock |
| I | I-1 | Sludge | 0.7 | Stock |
| J | J-1 | Sludge | 0.2 | Landfill |
| K | K-1 | Sludge | 0.1 | Landfill |
| | K-2 | Sludge | 0.6 | Landfill |

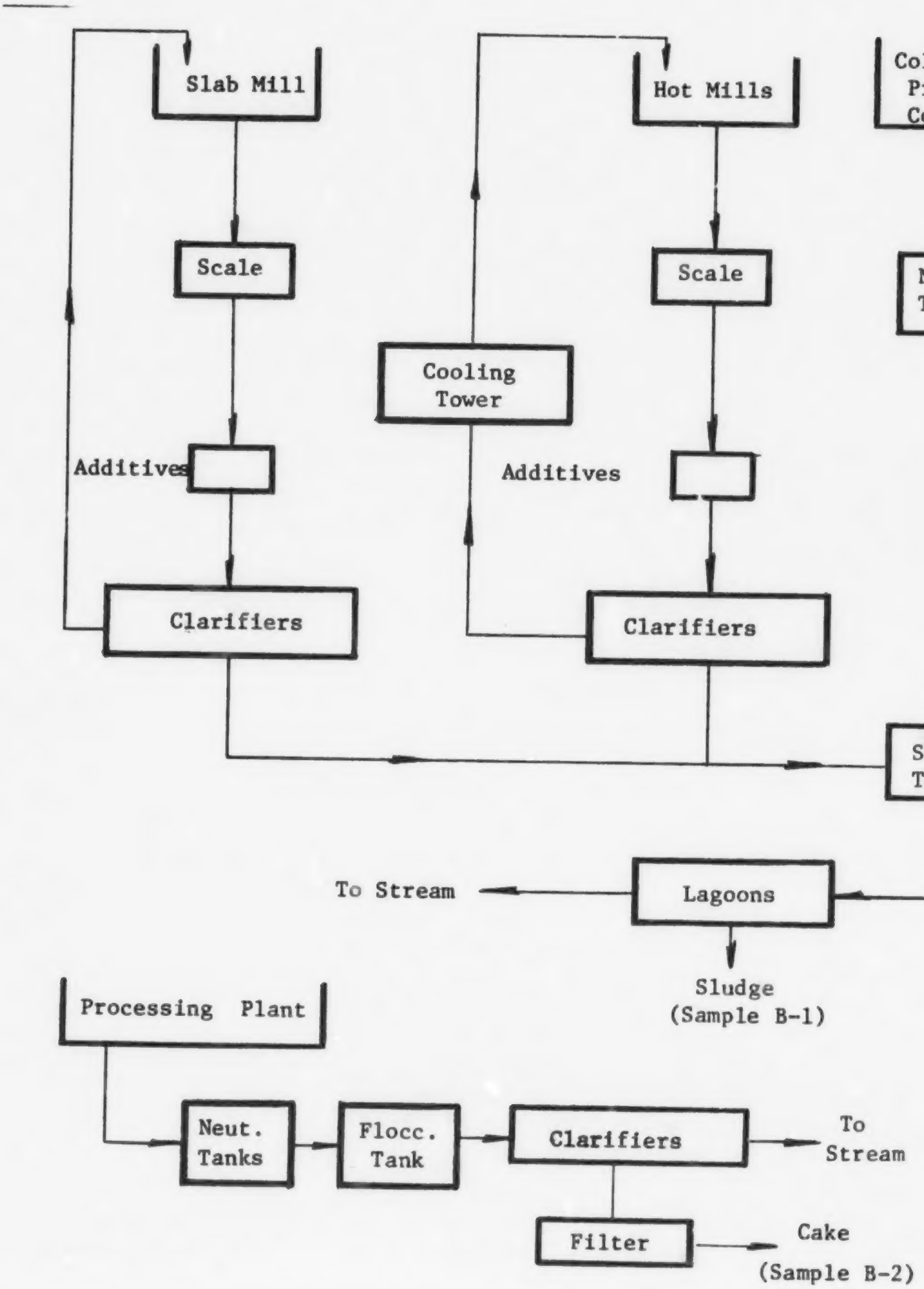
Slab Mill
Hot Mills
Cold Mills
Pickling
Coating
Scale
Scale
Neut.
Tanks
Cooling
Tower
Additives
Additives
Clarifiers
Clarifiers
Surge
Tank
To Stream
Lagoons
Sludge
(Sample B-1)
Processing Plant
Neut.
Tanks
Flocc.
Tank
Clarifiers
To
Stream
Filter
Cake
(Sample B-2)

Figure 3.14-I WASTE WATER TREATMENT PLANT SCHEMATIC - PLANT B

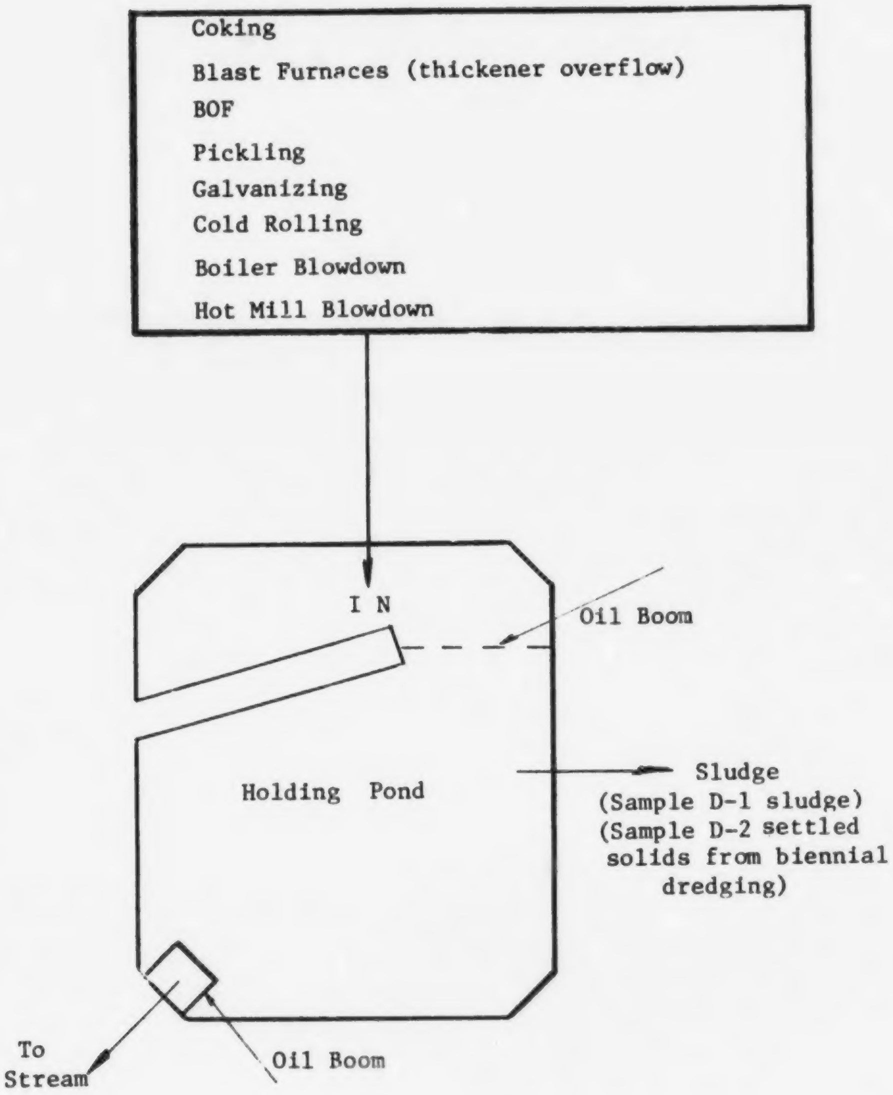
Coking
Blast Furnaces (thickener overflow)
BOF
Pickling
Galvanizing
Cold Rolling
Boiler Blowdown
Hot Mill Blowdown
I N
Oil Boom
Holding Pond
Sludge
(Sample D-1 sludge)
(Sample D-2 settled solids from biennial dredging)
To Stream
Oil Boom

Figure 3.14-II WASTE WATER TREATMENT PLANT SCHEMATIC - PLANT D

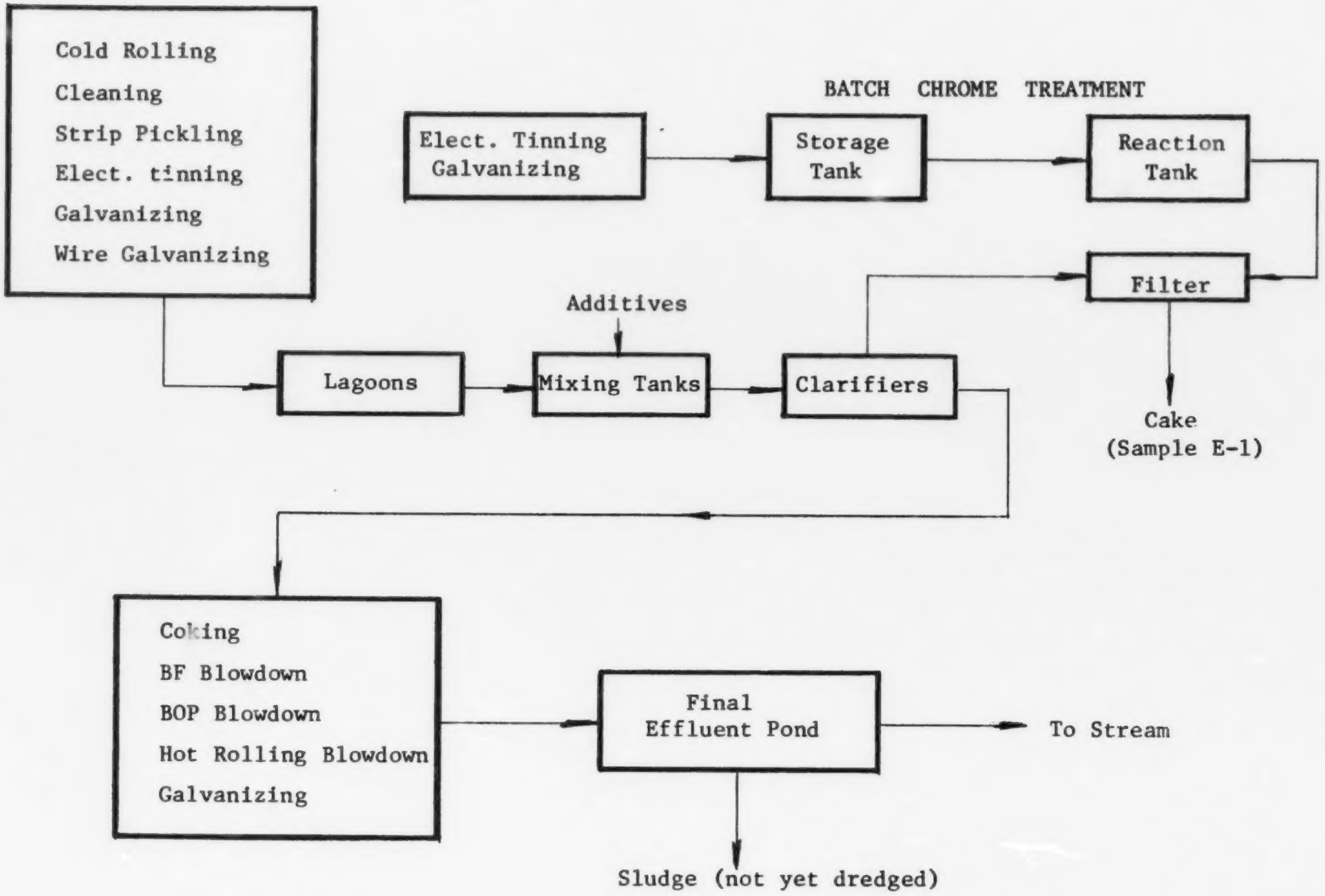
Cold Rolling
Cleaning
Strip Pickling
Elect. tinning
Galvanizing
Wire Galvanizing
BATCH CHROME TREATMENT
Elect. Tinning
Galvanizing
Storage Tank
Reaction Tank
Filter
Cake
(Sample E-1)
Additives
Lagoons
Mixing Tanks
Clarifiers
Coking
BF Blowdown
BOP Blowdown
Hot Rolling Blowdown
Galvanizing
Final Effluent Pond
To Stream
Sludge (not yet dredged)

Figure 3.14-III WASTE WATER TREATMENT PLANT SCHEMATICS - PLANT E

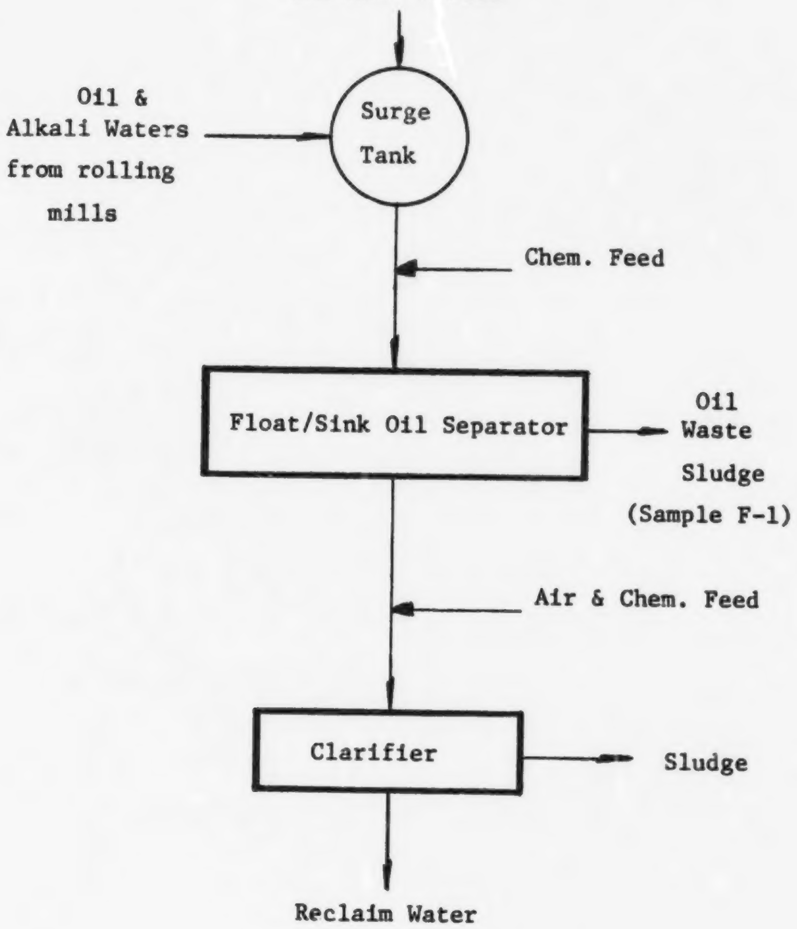
Miscell. Wastes
Oil & Alkali Waters from rolling mills
Surge Tank
Chem. Feed
Float/Sink Oil Separator
Oil Waste Sludge (Sample F-1)
Air & Chem. Feed
Clarifier
Sludge
Reclaim Water

Figure 3.14-IV WASTE WATER TREATMENT PLANT SCHEMATIC

PLANT F

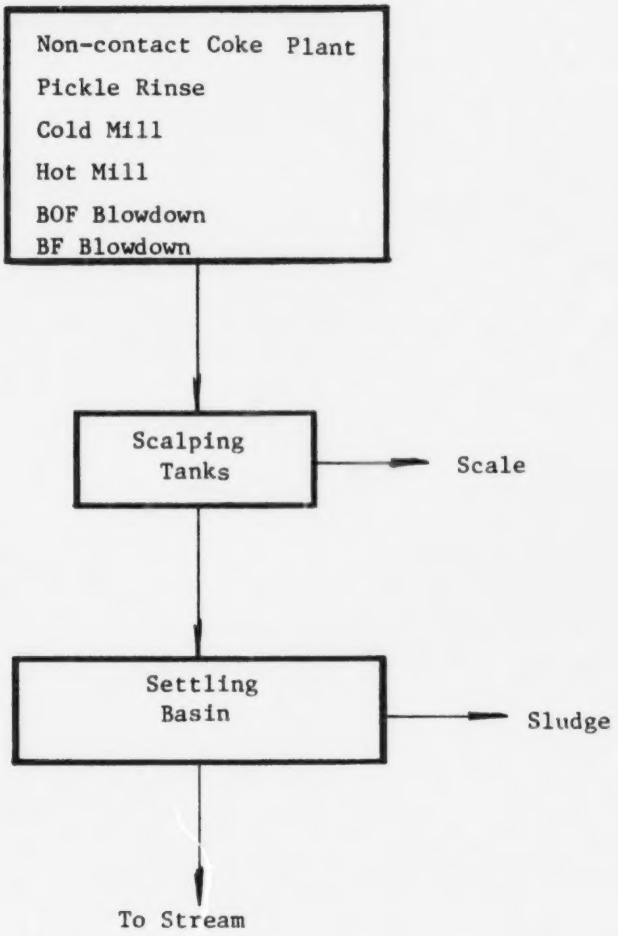
Non-contact Coke Plant
Pickle Rinse
Cold Mill
Hot Mill
BOF Blowdown
BF Blowdown
Scalping Tanks
Scale
Settling Basin
Sludge
To Stream

Figure 3.14-V WASTE WATER TREATMENT PLANT SCHEMATIC

PLANT G

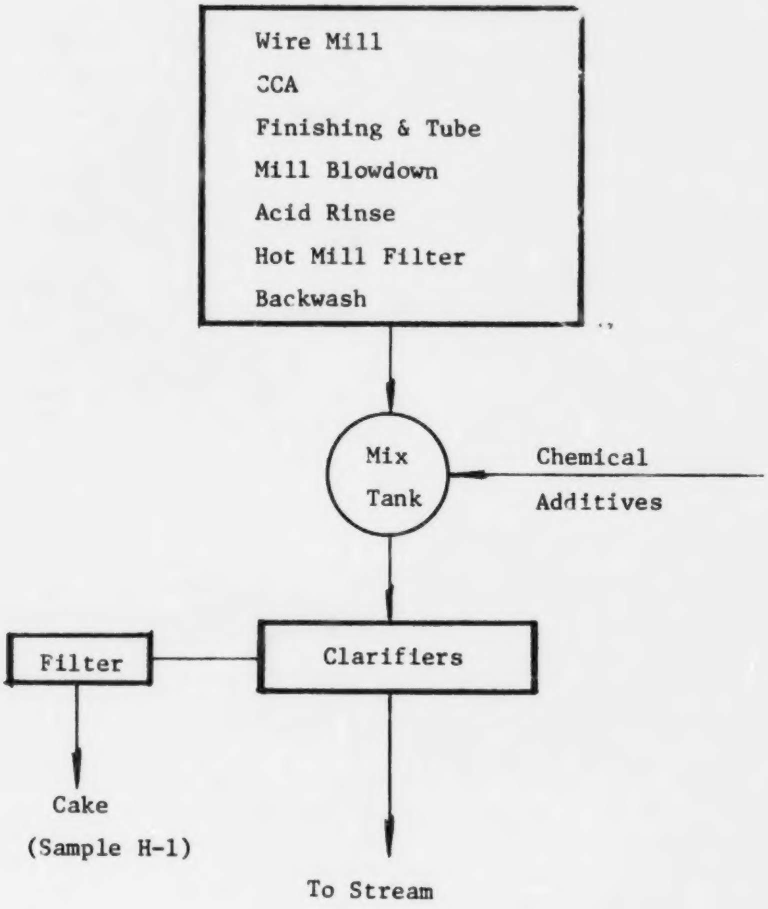
Wire Mill
CCA
Finishing & Tube
Mill Blowdown
Acid Rinse
Hot Mill Filter
Backwash
Mix
Tank
Chemical
Additives
Filter
Clarifiers
Cake
(Sample H-1)
To Stream

Figure 3.14-VI WASTE WATER TREATMENT PLANT SCHEMATIC
PLANT H

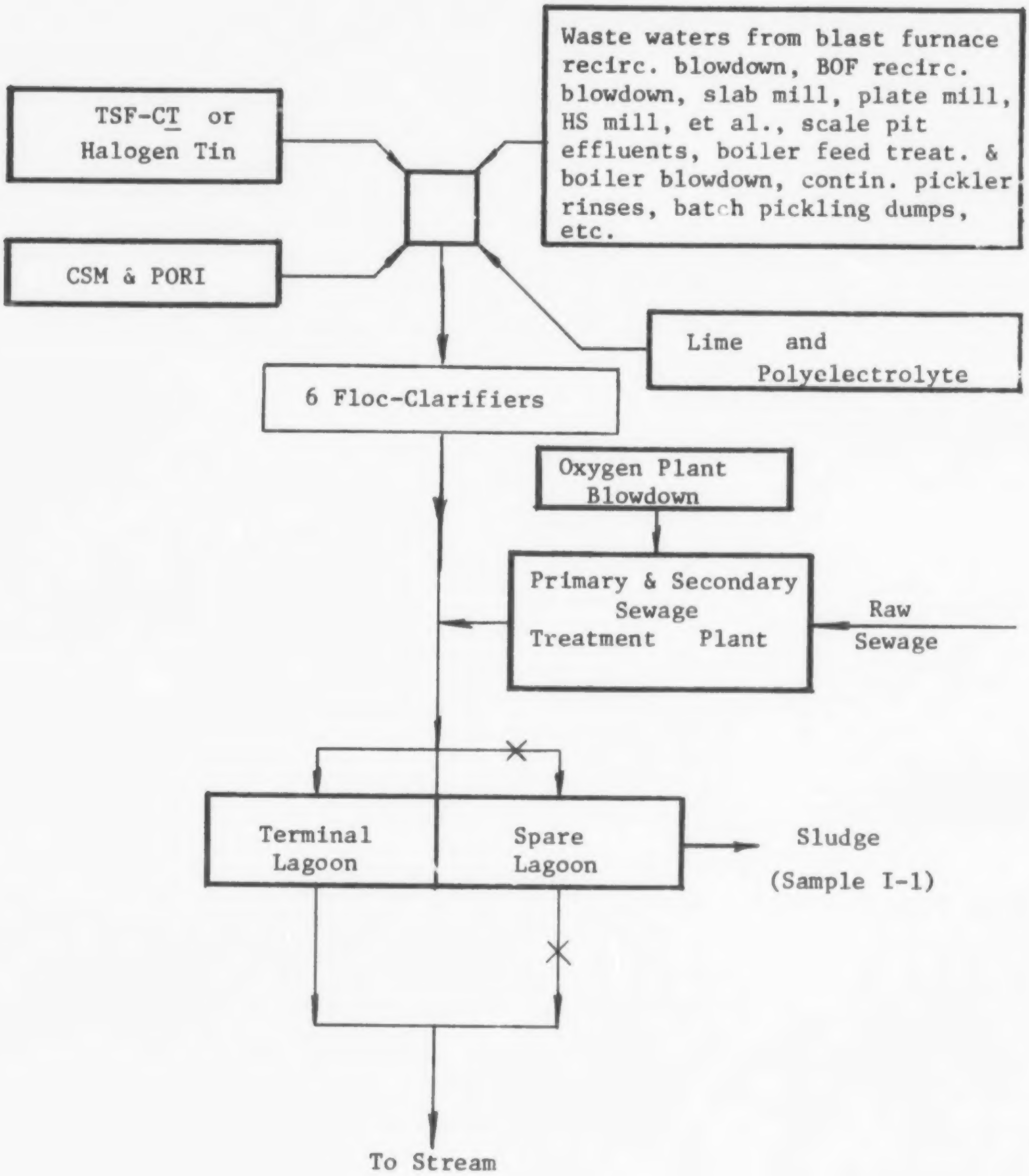
TSF-CT or
Halogen Tin
CSM & PORI
Waste waters from blast furnace recirc. blowdown, BOF recirc. blowdown, slab mill, plate mill, HS mill, et al., scale pit effluents, boiler feed treat. & boiler blowdown, contin. pickler rinses, batch pickling dumps, etc.
Lime and Polyelectrolyte
6 Floc-Clarifiers
Oxygen Plant Blowdown
Primary & Secondary Sewage Treatment Plant
Raw Sewage
Terminal Lagoon
Spare Lagoon
Sludge
(Sample I-1)
To Stream

Figure 3.14-VII WASTE WATER TREATMENT PLANT SCHEMATIC - PLANT I

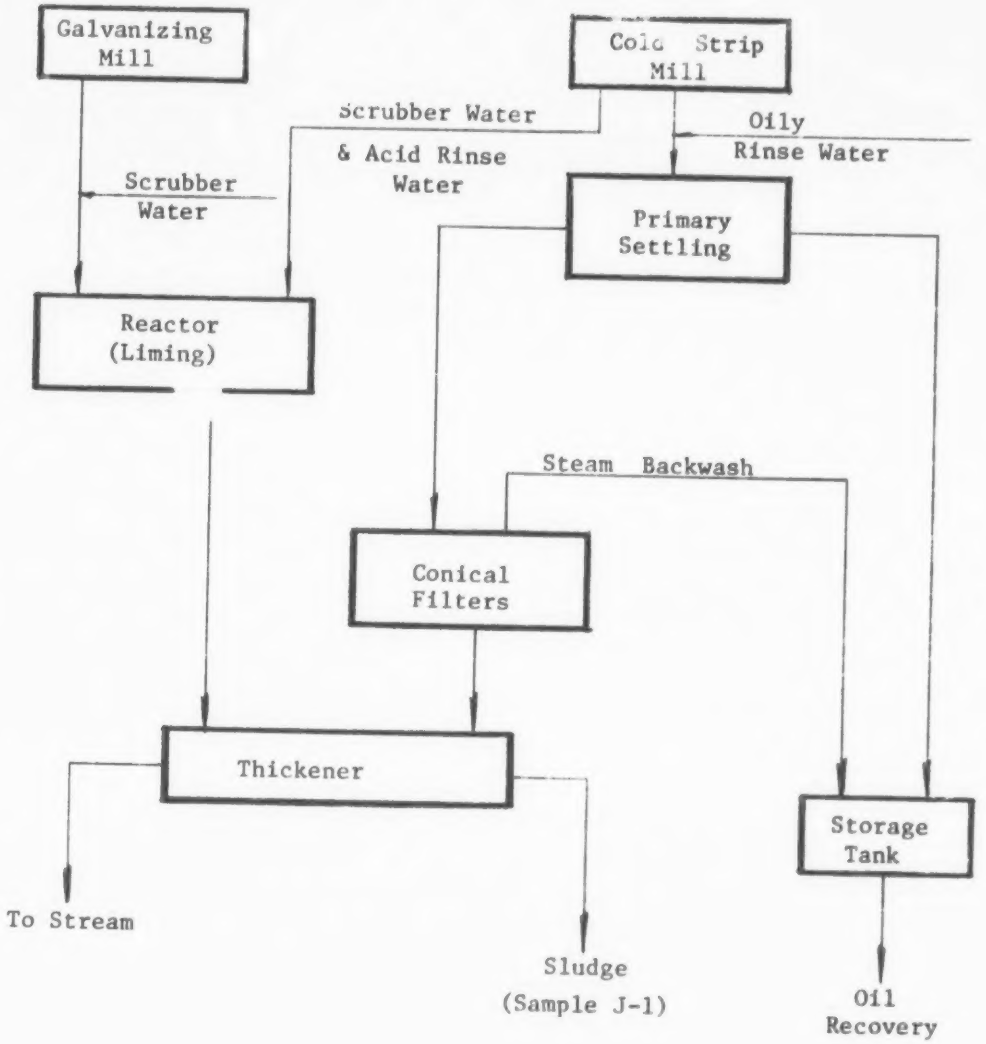
Galvanizing Mill
Cold Strip Mill
Scrubber Water & Acid Rinse Water
Oily Rinse Water
Scrubber Water
Primary Settling
Reactor (Liming)
Steam Backwash
Conical Filters
Thickener
Storage Tank
To Stream
Sludge (Sample J-1)
Oil Recovery

Figure 3.14-VIII WASTE WATER TREATMENT PLANT SCHEMATIC - PLANT J

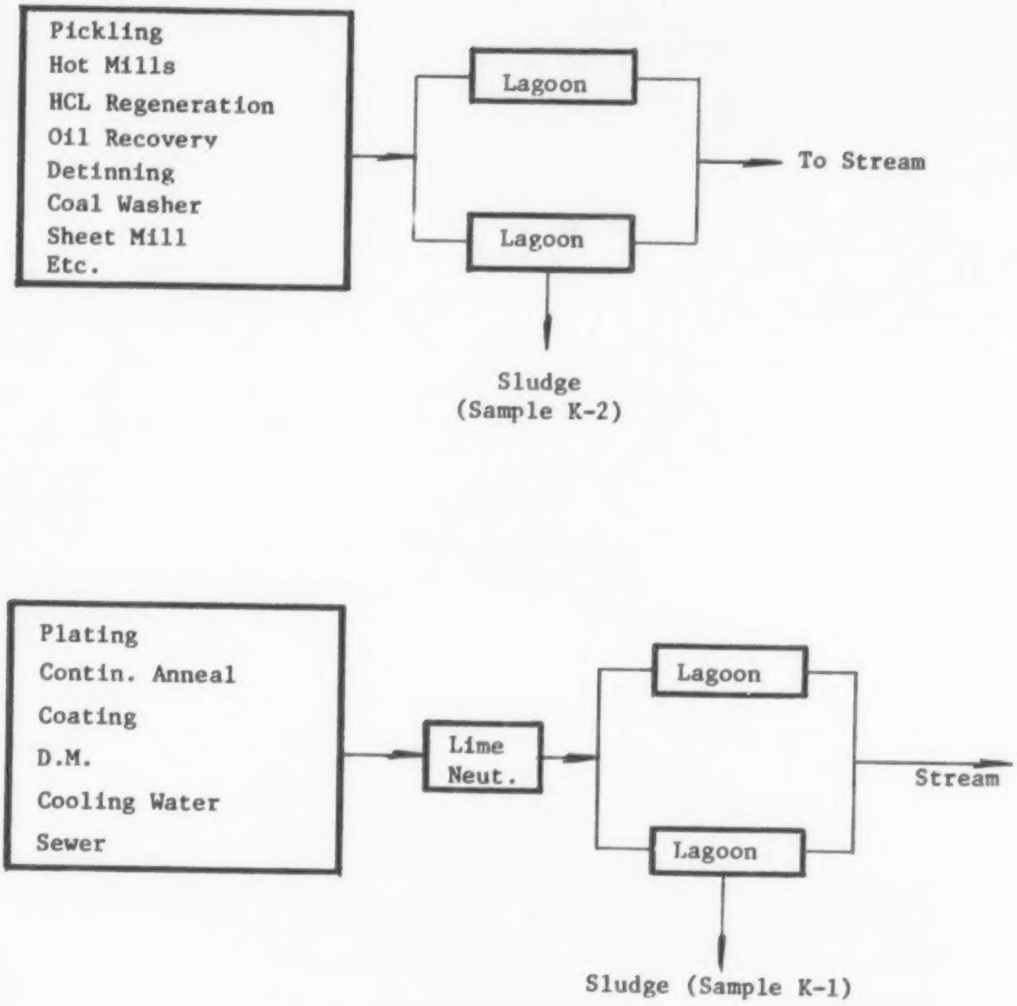
Pickling
Hot Mills
HCL Regeneration
Oil Recovery
Detinning
Coal Washer
Sheet Mill
Etc.
Lagoon
Lagoon
To Stream
Sludge
(Sample K-2)
Plating
Contin. Anneal
Coating
D.M.
Cooling Water
Sewer
Lime
Neut.
Lagoon
Lagoon
Stream
Sludge (Sample K-1)

Figure 3.14-IX WASTE WATER TREATMENT PLANT SCHEMATICS

PLANT K

## 3.15 SUBCATEGORY: MISCELLANEOUS OTHER OPERATIONS

Of the various operations covered in this section and listed in Table 3.15-1, only three produce any significant quantities of residues per ton of product produced.

Table 3.15-1 MISCELLANEOUS FACILITIES ASSOCIATED REGULARLY (OR OCCASIONALLY) WITH IRON AND STEEL MILL OPERATIONS

| Facility | Occurrence in Mill |
|---|---|
| Ore and raw material yards | Common |
| Coal washing | Rare |
| Lime kilns | Rare |
| Direct reduction | Rare (new technol.) |
| Pig casting operations | Common |
| Machine shops | Common |
| Maintenance shops | Common |

But even these operations (coal washing, lime kilns and direct reduction) are rare in steel mills. Therefore, the total quantities of residues produced in the U.S. in iron and steel mills from these three operations, compared with the quantities produced in the previous 14 subcategories, is negligible.

However, with the expected increased use of direct reduction, in combination with the new mini- and midi-steel mills, the quantities of residues generated with the various direct reduction processes will increase to significant levels in the next decade. The direct reduction processes are aimed particularly towards the processing of low grade ores with the more readily available non-coking coals(1). Presently, less than 2% of the world's iron and steel is produced by direct reduction(2).

In the direct reduction processes, both those using solid reducing agents (coals or coke breeze) and gaseous reductants (natural or snythetic gases), dusts and/or sludges are generated, depending on product cooling method and the pollution control installation used. None of the plants we had a chance to visit during our study had direct reduction facilities and, therefore, no residues were collected or analyzed.

The coal washing operations produce slimes, usually difficult to settle and stabilize. Their disposal present problems but the discussion of the disposal of these residues is not within the scope of our study.

Dusts are collected in the lime kiln pollution control facilities, but, again, they are not regarded as iron or steelmaking residues because useful applications can be found within the steel mill (e.g., in acid waste neutralization) or they are sold.

The ore and raw material yards including coal yards do not produce residues.

The pig casting operations, when used, produce some dusts and process waters with suspended solids (and "lime wash" residues used to prevent sticking of iron to the molds). Again, the quantities of residues generated are negligible and no samples were available from the mills we visited.

The machine shops and maintenance shops produce wastes but with the exception of their aqueous effluents (which are usually jointly treated with other wastes in the waste water treatment systems and contribute to those residues) no pollution control residues in any significant quantities are generated in these operations.

## 3.15 REFERENCES - MISCELLANEOUS OTHER OPERATIONS

1) The Making, Shaping and Treating of Steel - Ninth Edition. United States Steel Corporation, 1971.

2) Miller, J. R. Direct Reduction via Baden-Baden. I&SM, April 1976, pp. 27-30.

### 3.16 SUBCATEGORY: RECYCLING

The ideal solution to the problem of waste disposal, whether resulting from process or pollution control, is an economically viable recycle process whereby the waste can be effectively and efficiently reutilized. The residues generated in the pollution control facilities of the iron and steelmaking industry are no exception.

As was pointed out in Chapter II of this report and in previous sections of this chapter, significant quantities of pollution control residues are already recycled. In the U.S. close to 100% of the residues from coking, sintering and coating operations are recycled: 80% from blast furnace departments, 65% from the rolling mills, and about 50% from continuous casting operations. However, less than 25% of the residues from the three steelmaking, pickling and waste water treatment plant pollution control facilities are presently recycled (Table 3.16-1). These figures are based on data obtained (1) during our visits to the eleven steel plants, (2) from an extensive and comprehensive review of the literature, and (3) from meetings and discussions with operating and environmental personnel in the U.S. steel industry. Taking all of the information we were able to gather into consideration, we would estimate that about 60% of all of the residues generated in 1974 by pollution control operations in the mills was recycled.

Most of the pollution control residues presently recycled are either charged back directly into the blast furnace (e.g., $>5$ mm mill scale) or used as a feed in sintering or other types of agglomeration operations. The finest dusts and sludges with particle sizes of $<50$ microns are, in some cases, micro-pelletized before being used as sinter feed. Smaller quantities of residues are also sold for various uses.

Table 3.16-2 indicates the percent recycled and sold, "stocked" and dumped, based on the information supplied by thirteen U.S. steel mills

Table 3.16-1 ESTIMATES OF IRON AND STEEL INDUSTRY POLLUTION CONTROL RESIDUES IN THE U.S. IN 1974 AND COMPARISON OF % OF RESIDUES RECYCLED IN THE U.S. AND ABROAD

| | Residue Arising in U.S. (Million Tons) | % Recycled or Sold in | | | |
|---|---|---|---|---|---|
| | | U.S. | England | Germany | Japan |
| Coking | 1.0[a] (1.9-3.1[b]) | 98 | ~100 | ~100 | ~100 |
| Sintering | 0.9 | ~98[c] | ~100[c] | ~100[c] | ~100[c] |
| Blast furnace (iron) | 3.3 | ~80 | 50 | 85 | ~100 |
| Blast furnace (ferro-manganese) | < 0.05 | ~33 | NA | NA | NA |
| BOF | 1.7 | ~25 | 41 | 80 | ~100 |
| OH | 0.4 | < 20 | 15 | –[d] | – |
| EAF | 0.4 | < 10 | None | 100[e] | ~100[e] |
| Vacuum degassing | < 0.05 | Recycled only as part of other residues. | | | |
| Continuous casting | 0.2 | ~50 | NA | NA | ~100 |
| Rolling | 7.4 | ~65 | 87 | 80 | ~100 |
| Pickling | 0.4 | < 10 | 75 | NA | NA |
| Coating[f] | < 0.05 | 99+ | 99+ | 99+ | NA |
| Waste water treat. | 0.7 | < 10 | 30 | 20 | NA |
| Boilerhouse | NA | –[g] | – | – | – |
| TOTAL | ~ 16.5 | ~60 | 65 | 62 | 95[h] |
| (Reference: | | ( 1) | (76) | (64) | (65) |

a. Coke breeze (pollution control residues + coke dust).
b. Includes also coke pieces that passed the usually 1/2" screen.
c. Residues high in tramp elements are occasionally dumped or "stored."
d. No residue collected in 1974.
e. Recycled or "stored" for recycling.
f. Only coating and plating wastes.
g. By-product, not a residue; if throw-away sludge, no incentive to recycle.
h. Based on information from 3 mills, each with >10 million tons/year capacity.

### Table 3.16-2 RELATIVE QUANTITIES OF RESIDUES RECYCLED, SOLD, "STORED" AND DUMPED IN THE U.S.

(weight %)

| | Recycled or Sold | Main Routes of Recycling | Stored | Dumped |
|---|---|---|---|---|
| Coking | ∼98 | Sintering<br>Soaking pit[c]<br>Other[a] | 1-2 | <1 |
| Sintering | ∼98 | Sinter | 1-2 | 1-2 |
| Blast furnace (iron) | 77.4<br>(∼80) | Sinter | 9.3<br>(10) | 13.3<br>(10) |
| BF (ferromanganese) | ∼30<br>NA | BOF feed after agglomer. | | 70<br>NA |
| BOF | 24.3<br>(25) | Sinter | 25.5<br>(30) | 50.2<br>(45) |
| OH | 13<br>(15) | Sinter + other non-mill[c] | 29<br>(35) | 58<br>(50) |
| EAF | 5.6<br>NA | | 38.4<br>NA | 56<br>NA |
| Continuous casting | 50 | BF feed<br>Sinter | 25 | 25 |
| Rolling[b] | 70.4<br>(65) | BF feed<br>Sinter | 20<br>(30) | 10<br>(5) |
| Pickling | <10<br>NA | Sinter + other (chem.)[c] | 20<br>NA | 70<br>NA |
| Coating | ∼99 | Reprocessed by suppliers | - | <1 |
| Waste water treatment | <10<br>NA | Sinter | NA<br>NA | 90<br>NA |

[a] Processed by outside companies for non-iron or steelmaking purposes.

[b] Including scale and sludges.

[c] Minor quantities.

cooperating in our study. The figures in parentheses are the "best estimates," in which information obtained from the literature and various other sources were also taken into consideration, if different from those which are based solely on data from our study.

There are five main reasons for dumping (and storing) and not recycling the residues:

1) The fineness of the residues;
2) The difficulty in dewatering fine dust slurries and precipitates;
3) The high tramp element, especially zinc (Zn), lead (Pb), sulfur (S) and alkalis ($Na_2O + K_2O$), content of the residues;
4) The high oil content of some of the sludges and scales, and
5) The low metal (iron and/or non-ferrous) and carbon content of the residues, or the low useful material (acid or oil) content.

When the metal and other valuable ingredient content of the residue or waste is low, then recycling is usually not even considered.

To overcome the consistency or the difficulty in dewatering the residues, dewatering and agglomeration methods are used before the recycling of the residues, both in the U.S. and abroad. In dewatering the sludges, various filtration (vacuum or pressure) approaches or centrifuging are employed. For agglomeration, sintering is the most universally popular approach. However, pelletizing or micro-pelletizing is also used, sometimes in combination with sintering. Briquetting, while used in some operations, has not yet gained significant acceptance as a method for recycling steel mill residues.

Fine dusts are often wetted in pug mills(12) or mixed with slurries or sludges(3,4) before disposal or recycling. After wetting the dusts with the proper amount of water(2,22), steam(5), slurries(20) or sludges(3,4), the residues by themselves or in combination with raw materials, including other residues(6), can be reused, usually after conventional agglomeration, if the tramp content is low(1). Besides conventional sintering, briquetting(7) and pelletizing(2) are also used for agglomeration. The raw materials added to the residues (and other raw materials) can include binders and hardening agents such as bentonite(8,9,12,21,22), basic hydroxides(10), slaked lime(11,21), modified lime-silica combinations(10,13,14), cement(15,16,17) or thermal plasticizing resins(18).

To assure the proper composition of the residue raw material mixtures, computers are also used(19).

In another approach, the addition of fine residues to the coke-plant feed is recommended(23) as a means of recycling the residues. As a result, the coke is enriched with 2% iron. The iron subsequently is recovered during the burning of the coke in the ironmaking (BF) operations.

### Recycling of Zinc and Lead-Containing Residues

The afore-mentioned recycling procedures are and can be used, however, only when the zinc (Zn), lead (Pb) and/or oil content of the residues are low or tolerable. In Germany, 0.1%(24) to 0.2%(25) Zn, in Japan 0.25%(26), while in the U.S. and England usually less than 0.4% Zn + Pb-containing residues are recycled directly or through conventional sintering after dilution with other raw materials.

While the fine consistency of the dusts and sludges and the difficulties encountered in the dewatering of the slurries are no longer regarded as serious problems in recycling of residues, the high tramp element and oil contents are.

The "high" Zn and Pb content of the residues is regarded as the greatest problem in the recycling of iron and especially steelmaking dusts and sludges presently dumped or "stored." When the Zn and/or Pb-containing wastes are recycled, these elements are reduced and volatilized. Subsequently, the Zn and Pb vapors are oxidized and precipitated in the ducts of the sintering or blast furnace operations. In the blast furnaces, in addition, when precipitated in the upper (cooler) parts of the furnace this precipitation causes restrictions (e.g., "scaffolding") and difficulties in the operation of the furnace. Zinc can also attack the refractory lining by reacting with alumina in the lining and thereby causing additional damage to the furnace. The contamination of the produced iron with Zn is also undesirable. For the elimination of Zn and Pb and other interferences in the recycling of residues, various approaches are used (Table 3.16-3).

Table 3.16-3 METHODS OF BENEFICIATION OF IRON AND STEEL MILL ENVIRONMENTAL POLLUTION CONTROL RESIDUES(1)

I. Physical separations
    1. Gravity
    2. Magnetic
    3. Froth Flotation
    4. Skimming (of oil)
II. Pyrometallurgical methods
    1. Rotary kiln processes: SL/RN, Waelz, Krupp, Kawasaki
    2. Other processes:
        (a) Rotary hearth direct reduction
        (b) Chloridization or chlorination
III. Hydrometallurgical methods
IV. Electrometallurgical methods

For the recovery of iron and elimination of Zn and Pb interferences, thus far the physical separations, the hydrometallurgical methods and electrometallurgical approaches were found to be practically not feasible. However, several of the pyrometallurgical processes not only look promising(1,8,9,20,27,28,29,30) but are used successfully both in pilot-type and in full-scale facilities, mainly outside of the U.S., i.e., in Germany(9,31,32) and in Japan(33,34,35,36,37,38,39).

The oldest of these processes is the Waelz process. Originally developed for the reduction of Zn-bearing ores, in the last several years it has also been used for the recycling of Zn and Pb-containing iron and steelmaking pollution control residues(9,32,40). Variations of this process such as the Steel Company of Canada (STELCO)-Lurgi/Republic Steel Corporation-National Steel Company (SL/RN)(31,35,38,41,42,43,44), Krupp(45,46,47,48), and the Kawasaki(34,35,36,38) processes are also used for the recycling of Zn and Pb-containing residues. Further, other similar pyrometallurgical processes are still in the experimental stage(8,49,50,51,52,53,54,55).

In a present variation of the Waelz process, 80,000 tons of zinc and lead-containing residues are annually recycled in Duisburg-Wanheim (Germany) by Berzelius Metalhutten GmbH, an associate company of Lurgi(9,32).

In other processes such as the previously mentioned SL/RN process, the Lurgi-Nippon Kokan K.K. process, the Krupp and Kawasaki processes, traveling grate pre-heaters are used to pre-indurate and pre-reduce the residues before the rotary kilns to aid in the removal of Zn and Pb.

All of the above-mentioned processes, including the Waelz, as well as the Vlnaty(59) and the Ferro-Tech, Inc.(20), processes, are based on the reduction by carbon. The Ferrocarb(56) reduction process utilizes, in addition to carbon, an hydrocarbon as the binder.

The Ferro-Tech process(20) uses a rotating hearth furnace with four zones, to which the "green" balls are fed in a thin layer. The four zones are separated by baffles to achieve proper drying, pre-heating, reducing and indurating at various temperatures and in various atmospheres. The Zn and Pb are volatilized in the reducing zone from which the gases are handled separately through a baghouse for Zn and Pb recovery.

In the Berzelius operation the properly sized and, if necessary, dewatered residues are mixed with coke breeze (and/or coal dust) and usually also with lime. The mixture, after pelletization, is introduced into the rotary kiln. Additional coke dust or coal dust is added to the kiln to supply additional heat and to keep the atmosphere reducing. In the kiln the Zn and Pb are volatilized (after reduction) during the induration (heat treatment) and subsequently oxidized in the air to form the "Waelz dust" consisting of the oxides of Zn and Pb and other dust particles generated during the process (Table 3.16-4). After cooling, these dusts are recovered in electrostatic precipitators. The end product from which 90-95% of the Zn and Pb are removed,is also 90-95% reduced with respect to iron.

To avoid the oxidation of the "sponge iron" product in the air, it is rapidly cooled. Screening is used to separate the fines from the final product. Magnetic separation is used to recover additional iron values, after which the reusable char (usually > 1 mm) is screened out and recycled with the coke breeze or coal dust.

The Dravo-Vlnaty system uses a pre-heated inert material as a solid heat carrier and a shaft furnace system for Zn and Pb removal(58).

Obenchain Corporation also has developed a Zn and Pb removal technology(10) using a rotary kiln which is used in conjunction with their CHOR pelletizing system.

Dravo Corporation's in-house research and experience and this study indicates that the selection of the recycling process for the residue will depend on the tramp element content, the consistency and the quantities of the various residues to be processed.

Table 3.16-4 CHEMICAL COMPOSITION OF WAELZ OXIDES

(Percent by Weight - dry basis)

| Sample No. | Zn | Pb | Tot. Fe | C | S | CaO | MgO | $Na_2O$ | $K_2O$ | $SiO_2$ | TiO + $Al_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1(27) | 64.9 | 7.4 | 1.3 | 2.9 | 1.2 | 0.4 | 0.14 | 0.54 | 0.60 | 0.4 | 0.15 |
| 2(27) | 51.4 | 7.6 | 3.6 | 12.0 | 2.8 | 0.6 | 0.25 | 0.60 | 0.55 | 1.5 | 1.0 |
| A(57) | 40/ 50 | 5/ 10 | 1/ 5 | 1 - 3 | 0.6/ 0.8 | NA | NA | NA | NA | NA | NA |
| B(9) | Zn + Pb > 40% | | | | | | | | | | |

Several American steel corporations are studying the different processes they could use in an economically and technically feasible way to recycle their presently "stored" or dumped residues.

## Recycling of Oily Residues

Another significant quantity of pollution control residues presently dumped or "stored" originates in the rolling operations. While roughly 70% of the scale, including fine scale, is recycled or sold, most of the sludges from the secondary and, in some cases, tertiary treatment operations are dumped or "stored." According to our estimates of the roughly 7.4 million tons of rolling residues, approximately 3.2 Mt were still stored and dumped, mainly because of the high oil content (especially "volatile" oil content). Due to the fine consistency of the solids in (and the oil absorbing properties of) the sludges generated in the post-scale pit water clarification operations, it is often difficult to separate the oil from the iron-rich residues.

The oil content of the residues presents a two-fold problem in the recycling of the rolling residues. When these oils are volatilized during recycling (e.g., in pelletizing or sintering operations): (1) they can cause fire in the electrostatic precipitators or difficulties in baghouse operations, and (2) the escaping oil vapors or their combustion products cause air pollution.

Most of the oil is easily removed from the rolling mill effluents by various types of oil skimmers. The oil after separation is usually recovered and reused. However, the oil cannot be separated from the sludges by simple settling and skimming operations. As described in Section 3.10, Rolling, various approaches are used for the separation of oil from the aqueous phase and the residues.

In the successful operations, the oil is separated from the wastes usually before the final sludge settling operations. Various chemical treatments(59,60,61), including solvent extraction of the oils(62) and coalescers(62), and evaporation(63) are used. However, when the oil is not removed before the final settling of the residues, then the oils have to be burned during the recycling (e.g., sintering or pelletizing) and/or scrubbed out from the off-gases before they can reach the dust control equipment and/or the atmosphere. This approach, however, is still considered experimental(64).

## Recycling of Pickling Wastes

The recycling of pickling acid wastes or residues generated during the neutralization of the waste acids and rinse waters presents a special case. Today almost one-half million tons of residues are generated in the U.S. (.4 million tons in acid neutralization and 0.1 million tons in joint treatment facilities). Most of this pickling residue is being dumped or "stored." However, the generation of these residues can be eliminated if the hydrochloric acid is regenerated and the sulfuric acid recovered, and commercially valuable by-products are produced in place of residues.

The recovery of values from the hydrochloric acid and sulfuric acid pickling liquors, besides economic considerations, is generally not regarded as a problem because, among others, the Dravo, Lurgi, Ruthner, etc., pickling waste regeneration and recovery processes are well established and have been successfully used for many years.

In Europe (especially in Austria and Germany) and in Japan essentially all waste pickling acids are reprocessed and the by-products (iron oxide, iron sulfate, iron chloride) and the acids are either sold or reused within the mills.

Occasionally when the purity of the iron oxides do not meet customer specifications and, therefore, the residue cannot be sold, it is balled and can be recycled through the furnace operations.

The sulfuric acid recovery(66,67,68) and hydrochloric acid regeneration(69,70,71,72,73) processes have been used with success for many years. However, the recycling of some mixed acids used in the pickling or surface treating of alloy and stainless steels is just becoming more generally accepted.

A solvent extraction process was developed by Stora Kopparbergs in Sweden for nitric-hydrofluoric acid mixtures. The process regenerates both acids from the spent pickle liquor by recovering about 95% of the nitric acid and 70% of the hydrofluoric acid(74,75).

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# APPENDIX

## METHODS USED IN ANALYZING STEEL INDUSTRY POLLUTION CONTROL RESIDUES

### Initial Sample Preparation

Upon receipt, the samples were dried at 90° C until a constant residue weight was obtained. Due to the widely varying water content of similar samples, the lack of knowledge of specific sampling conditions, and the partial dehydration of the samples during transport and storage, the moisture content of the samples was not quantitatively determined.

The second step in the preparation for chemical analysis was the removal of oil and grease from the samples by the Soxhlet extraction method using Freon 113* as the extracting fluid. The Freon had been previously purified by distillation. The residue recovered from the Freon after the extraction was weighed and reported as oil and grease content on a moisture-free basis. The de-oiled solids were used for all subsequent analyses, the results of which were reported on a moisture-free, greaseless, oil-less basis.

### Chemical Analyses

Atomic absorption analyses were used for the determination of aluminum, antimony, arsenic, calcium, chromium, lead, magnesium, manganese, potassium, selenium, soidum, tin and zinc. The samples were dissolved in mineral acids, and, if necessary, the residue was treated with hydrofluoric acid and fused with sodium carbonate.

A separate sample was used for the sodium analysis. In the dissolution of this sample for soidum analysis, any residue remaining after the acid dissolution was treated with hydrofluoric acid, and then leached with hydrochloric acid instead of fused with sodium carbonate.

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* Registered Trade Mark of E. I. DuPont DeNemours & Company

Standard atomic absorption analytical techniques were employed(1). The samples were matched to the standards, and the most sensitive absorption wavelengths were used in conjunction with the proper flame type, either air acetylene or nitrous oxide acetylene. A deuterium arc background corrector was used in the analyses of the lower wavelength elements: arsenic, selenium, antimony and tin(2).

Gravimetric analyses was used for the determination of silica, carbon and sulfur. Silica was determine by volatilization as silicon tetrafluoride after dehydration by fuming perchloric acid(3). Carbon and sulfur were determined by combustion in an oxygen stream, using a resistance furnace as the heat source. The carbon dioxide formed from the combustion of the carbon was absorbed on an Ascarite bulb(4). On a separate sample, the sulfur dioxide formed was absorbed and oxidized in a hydrogen peroxide solution, then precipitated as barium sulfate(5).

The only volumetric technique employed was for the analysis of total iron content. The samples were fused with a sodium peroxide - sodium carbonate mixture in a zirconium crucible. After dissolution of the melt and reduction of the iron, a standard cerate solution was used to determine the iron content(6). When the manganese content was above 1%, the manganese was removed before the iron titration.

Cyanide determination in selected samples was performed by a cyanide specific ion electrode method(7).

## Particle Size Analysis

The dried de-oiled samples were sieved through 10 μ, 20 μ and 325 mesh screens by two methods involving sonic vibrations. In one method, a vibrating air column was used to do the sieving and in the other an ultrasonic alcohol bath was used.

If the above screenings indicated that there was more than 20-30% of +325 mesh material in a particular residue, another screening was performed. Here, another portion of the dried and de-oiled sample was wet-screened through a 325 mesh screen and the +325 mesh fraction dried and dry-screened using a Tyler Ro-Top (10 minutes) to ascertain the quantity and sizing of the larger-than-325-mesh particles. This accounts for the dual screening figures given for some samples, as indicated in the various tables throughout this report.

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